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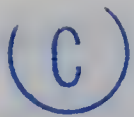
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INORGANIC PHOSPHORUS FORMS IN ALBERTA SOILS

by



THUNDATHILTHEKKETHIL GEORGE ALEXANDER

B. Sc. (Agr.)

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Inorganic Phosphorus Forms in Alberta Soils" submitted by Thundathilthekkettil George Alexander in partial fulfilment of the requirements for the degree of Master of Science.

A B S T R A C T

Inorganic phosphorus forms in eighteen profiles of Alberta soils, three each of Maleb, Beaverhills, Breton, Boundary, and Heart plus one each of Rimbey, Winterburn, and Glory (high in available phosphorus), were fractionated by the modified Chang and Jackson procedure. The forms determined were calcium-bound (Ca-P), aluminum-bound (Al-P), iron-bound (Fe-P), and occluded (Occl-P) phosphorus.

Ca-P varied from 1 to 442 ppm and it was the dominant form in Maleb, Beaverhills, and the C horizons of Glory and Breton Series. With the exception of Boundary, Ca-P decreased with depth in all the soils. Al-P ranged from 2 to 398 ppm. There was a tendency for Al-P to decrease with depth in all the series except Heart, where it accumulated in the Bf horizon. Fe-P varied from 5 to 260 ppm and it decreased with depth in all the series except Boundary and Heart. The series high in available phosphorus had high amounts of Al-P and Fe-P in their surface horizons. Occl-P varied from 1 to 174 ppm. Occl-P decreased with depth in the Chernozemic soils and with the exception of the Heart Ae horizon, other Podzolic soils were comparatively high in this form.

There was no apparent relationship between the distribution of soil separates and inorganic phosphorus forms. Al-P and Fe-P were the predominant forms in acid soils, while alkaline soils were high in Ca-P. Parent material and

climate seemed to have an effect on the distribution of inorganic phosphorus forms.

Residual plus organic phosphorus (total phosphorus minus total inorganic phosphorus forms) varied from 5 to 610 ppm and it constituted 4 to 75% of the total phosphorus. It is thought that most of the phosphorus in this form is in organic combination. Total phosphorus ranged from 18-930 ppm. Correlations between available phosphorus (Miller and Axley, and Olsen methods) and Ca-P, Al-P, and Fe-P suggested that Al-P and Fe-P may be the major sources of available phosphorus in the soils studied.

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INTRODUCTION

Phosphorus has a unique position in the field of soil fertility. Though phosphorus is required by plants in smaller amounts than nitrogen and potassium, shortage of available phosphorus exists in many soils. A thorough knowledge of the distribution of inorganic phosphorus forms and the conditions under which these become available to plants would be useful in the study of availability of soil phosphorus. It would be desirable to study the nature and distribution of inorganic phosphorus forms in Alberta soils before any detailed investigation in this field is undertaken.

Phosphorus is present in the soil in two general forms, inorganic and organic. In the organic form, phosphorus is found in nucleic acids, phospholipids, and inositol phosphates. The predominant inorganic phosphorus forms in soils are: water soluble plus loosely bound, aluminum-bound, iron-bound, calcium-bound, and occluded phosphorus. Currently, information on inorganic phosphorus forms receives extensive use in soil genesis and soil fertility studies.

This project was undertaken with the following objects:

- A. To study the amount and distribution of inorganic phosphorus forms in Alberta Soils.
- B. To correlate the distribution of inorganic phosphorus forms in soils with physical and chemical properties.

REVIEW OF LITERATURE

A. Phosphorus Studies on Alberta Soils

Doughty (1931) conducted phosphorus studies on some Alberta soils and reported that the soils were in general high in water soluble or available phosphorus, though many of them did respond to phosphatic fertilizers. Iron, aluminum, and organic compounds were found to be responsible for most of the soluble phosphorus. He did not find any close relationship between total and available phosphorus. Superphosphate alone, or lime and superphosphate increased the soluble or available phosphorus.

Later, Odynsky (1934, 1936) studied the various horizons of typical Brown, Black, and Grey profiles in an effort to determine the solubility and distribution of phosphorus. He classified the soil phosphorus into four forms:

1. Easily soluble--fraction soluble in $0.002N\ H_2SO_4$.
2. Difficultly soluble--fraction soluble in $2N\ H_2SO_4$ minus easily soluble fraction.
3. Organic--the difference between phosphorus extracted by $2N\ H_2SO_4$ before and after ignition.
4. Insoluble compounds.

Easily soluble phosphorus was found to be present in much larger amounts in the B_1 , B_2 , and C horizons of the Brown

profile than in the A_1 horizon. In the Black profiles, it was present in small to medium amounts in the A and B_1 horizons and increased to form a large percent of the total phosphorus in the B_2 or lime horizons. The Grey profiles had a medium proportion of easily soluble phosphorus in their A_0 , A_1 , and A_2 , a small amount in the upper B_1 , and large amounts in the lower B_1 , upper B_2 , and lower B_2 horizons. Difficultly soluble phosphorus content was fairly low in all horizons of the Brown and Black profiles. The Grey profiles showed a small proportion of difficultly soluble phosphorus in the A_0 horizon, much greater proportions in the A_1 , A_2 , and upper B_1 horizons, and small proportions below the upper B_1 horizons. Organic phosphorus occurred in large amounts in the surface horizons, but below these the amounts of organic phosphorus diminished to very small quantities in the B_2 and C horizons. Amounts of phosphorus varying from 0 to 20 percent remained insoluble after ignition and repeated extractions with $2N\ H_2SO_4$.

These two early studies were followed by some investigations on the nature and amount of organic phosphorus: Thomas and Lynch, 1960; Dormaar, 1961, 1963; Dormaar and Webster, 1963 a, 1963 b; Dormaar, 1964a, 1964 b; and Dormaar and Webster, 1964.

B. Fractionation of Soil Phosphorus

As early as 1906, Fraps used mineral acids of varying concentrations to differentiate aluminum, iron, and calcium

phosphates in soils. Fisher and Thomas (1935) proposed an extraction method to differentiate four phosphorus forms on the basis of their solubility in selected buffered acidic solutions:

1. Amorphous and finely divided crystalline phosphates of calcium, magnesium, and manganese.
2. Amorphous phosphates of aluminum and iron.
3. Phosphorus adsorbed upon hydrous oxides and those present in the form of apatite.
4. Phosphorus present as crystalline phosphates of aluminum and iron.

However, Dean (1937, 1938) was the first to attempt a systematic and complete fractionation of soil phosphorus. He grouped the phosphorus compounds of soils into four broad categories.

1. Inorganic alkali soluble (0.25 NaOH, followed by decolorization)--iron and aluminum phosphates and small amounts of mono and dicalcium phosphates if they are present in the soil.
2. Organic alkali soluble (0.25N NaOH, followed by oxidation)--definite organic combinations of phosphorus.
3. Acid soluble (0.5N H_2SO_4) but alkali insoluble--apatites and tricalcium phosphate.
4. Insoluble compounds--unknown composition.

He found that part of the total soil phosphorus which was not removed by the combined alkali and acid extractions in many instances constituted the largest fraction of the soil phosphorus.

Williams (1937) grouped phosphorus compounds in soil on the basis of their solubility in NaOH solutions (2 to 20 percent) into:

1. Soluble--phosphorus in combination with sesquioxides, organic phosphorus, exchangeable phosphorus of clay complex, phosphorus of calcium compounds such as mono and dicalcium phosphates, and phosphorus of water soluble compounds.
2. Insoluble--phosphorus compounds of the apatite class.
3. Doubtful--phosphorus in interior of clay lattice and phosphorus of titanium compounds.

Later Chirikov and Volkova (1941) classified soil phosphorus into five forms:

1. Fraction soluble in water or H_2CO_3 --alkali phosphates, acid phosphates, diphosphates of calcium, magnesium, trimagnesium phosphate, and some phosphorites.
2. Fraction soluble in 0.5N HOAc--some apatite, phosphorite, and salts of alcohol phosphoric acids and sugar phosphoric acids.
3. Fraction soluble in 0.5N HCl--phosphorite, apatite,

aluminum and iron phosphates, and some of the more basic phosphates of iron, and phytin.

4. Fraction soluble in 0.2N NaOH--nucleins, nucleoproteins, and similar compounds of humic acids.
5. Fraction insoluble in any of these solvents--titanium phosphate and phosphorus compounds of the unweathered minerals of the parent material.

The initial extraction in the fractionation procedure proposed by Dean was made with 0.25N NaOH. Here, soluble or exchangeable calcium and magnesium interfered with the extraction of phosphorus by alkalies. To overcome this, Ghani (1943 a) modified the procedure by extracting first with 0.2N HOAc, then with 0.25N NaOH until the phosphorus extracted was very low, and finally with 2N H₂SO₄. Five fractions were obtained as follows:

1. HOAc soluble--mono, di, and tricalcium phosphates.
2. Alkali soluble inorganic--aluminum and iron phosphates.
3. Alkali soluble organic phosphorus.
4. H₂SO₄ soluble phosphorus of the apatite type.
5. Insoluble phosphorus.

Further, Ghani (1943 b) modified the procedure by adding 8-hydroxyquinoline to the HOAc to check readsorption of phosphorus by aluminum and iron.

In an attempt to simplify the above procedure, Williams (1950) grouped compounds of soil phosphorus into three major groups:

1. HOAc - 8-hydroxyquinoline extractable--water soluble phosphates, calcium phosphates, hydroxy and carbonate apatite, manganese phosphates and to some extent chlor and fluorapatites.
2. NaOH extractable--
 - a) Inorganic--adsorbed phosphate, basic aluminum and iron phosphates, and titanium phosphate.
 - b) Organic phosphorus.
3. Insoluble in either extractants--chlor and fluorapatites, crystal lattice phosphorus, resistant phosphate minerals such as turquoise, monazite, and amblygonite.

However, there remained an insoluble portion of soil phosphorus unextracted in all these fractionation schemes. It remained for Chang and Jackson (1957) to formulate a complete and systematic inorganic soil phosphorus fractionation procedure based on previous studies: Dean, 1938; Dickman and Bray, 1941; Ghani, 1943a; Williams, 1950; Turner and Rice, 1952; and Aguilera and Jackson, 1953. Six forms of inorganic phosphorus were obtained by treating the soil with the following reagents successively:

1. 1N NH_4Cl extractable--water soluble plus loosely bound phosphorus.

2. 0.5N NH_4F (pH 7.0) extractable--aluminum-bound phosphorus.
3. 0.1N NaOH extractable--iron-bound phosphorus.
4. 0.5N H_2SO_4 extractable-calcium-bound phosphorus.
5. 0.3M sodium citrate-sodium dithionite extractable--reductant soluble iron-bound phosphorus.
6. 0.5N NH_4F and 0.1N NaOH extractable=occluded aluminum-iron-bound phosphorus.

Soil phosphorus fractionation studies were also attempted by the following workers: Stelly and Pierre, 1942; Allaway and Rhoades, 1951; Godfrey and Riecken, 1954; Bhangoo and Smith, 1957; Saunders, 1957; and Patel and Mehta, 1961.

C. Modification of the Chang and Jackson Procedure

There have been several modifications in the Chang Jackson procedure. A brief review of the major modifications follows:

1. Fife, 1959a, 1959b

From the results obtained in the study of phosphate solubility in systems containing $\text{Fe}(\text{OH})_3$, Fife concluded that at pH 7.0 (Chang and Jackson procedure step 2) the effects of secondary reactions, obscuring the true aluminum-bound phosphorus value were likely to be most pronounced. It was shown that the fluo-ferrate ion did not completely dissociate until the pH rose

to a value of approximately 8.0 in 0.5N NH_4F . Phosphate solubility in systems containing $\text{Fe}(\text{OH})_3$ was shown to reach a minimum value in the vicinity of the neutral point. Therefore it was concluded that a satisfactory delineation of the aluminum-bound soil phosphorus was unlikely to be attained by the use of 0.5N NH_4F at pH 7.0. He suggested that the use of a fluoride solution sufficiently alkaline to inhibit the read-sorption of phosphate by free iron oxides might result in an improved delineation of aluminum-bound phosphorus, and, therefore, he recommended a pH of 8.5 for NH_4F solution. One advantage of employing the reagent at pH 8.5 is that it is sufficiently well buffered to resist pH change in the presence of most soils. And at this pH, iron phosphate in soils displays a marked resistance to alkaline hydrolysis.

2. Glenn et al., 1959

They studied the selectivity of the different extraction solutions used by Chang and Jackson with natural soil samples and synthetic and natural phosphate minerals. The essential changes were as follows:

- a) Use of 0.5N NH_4F at pH 8.2.
- b) Reversal of the order of extraction of reductant soluble iron-bound phosphorus and calcium-bound phosphorus.
- c) Removal of organic phosphorus from the sodium dithionite extract by shaking with activated charcoal, in case of soils high in organic matter.

- d) Grouping of occluded aluminum-bound phosphorus and occluded aluminum-iron-bound phosphorus. The residue remaining after sodium citrate-sodium dithionite extraction was given a sodium hydroxide treatment to remove the total occluded aluminum-iron-bound phosphorus.

3. Khin and Leeper, 1960

They noticed that keeping the pH of NH_4F solution at either 7.0 or at 8.5 does not correct the errors involved in separating aluminum phosphate from iron phosphate in soils. At a higher pH, the phosphate ion is displaced from the iron phosphate by hydroxide ion, giving too high a value. In addition, an opposite source of error is possible. The phosphorus extracted by NH_4F will again be adsorbed by $\text{Fe}(\text{OH})_3$ or calcium in the case of carbonate soils when the pH is 8.5; if so, part of the extracted aluminum phosphate will be considered as the iron phosphate in NaOH extraction or as the calcium phosphate in H_2SO_4 extraction. According to them, widening the ratio of the volume of the extractant to the soil may reduce but cannot eliminate these errors.

Further, they doubted the degree of accuracy in determining the principal calcium phosphates by 0.5N H_2SO_4 extraction (after successive treatment of soil with 1N NH_4Cl , 0.5N NH_4F , and 0.1N NaOH). When the soil is treated with 0.5N H_2SO_4 , a reprecipitation of phosphorus by the soil is possible as a result of the acid soluble iron entering simultaneously into solution, that is, a so-called secondary phosphorus

adsorption takes place. However, this error is avoided by the reversal of the order of extraction of reductant soluble iron phosphate and calcium phosphate (Glenn et al., 1959).

4. Fiskell and Spencer, 1964

There is enough evidence to show the presence of dicalcium phosphate dihydrate (DCPD) and tricalcium phosphate (TCP) in soils. Fiskell and Spencer observed that NH_4Cl is an unsatisfactory extractant to dissolve DCPD and TCP formed after the application of triple superphosphate in soils. Therefore, they employed 1N NH_4OAc buffered to pH 4.8 with HOAc instead of 1N NH_4Cl used in the original sequential extraction.

5. Smith, 1965

He applied a correction factor, calculated from percent recoveries of increasing amounts of standard phosphorus added to the NH_4F extractant, for an accurate separation of aluminum phosphate from iron phosphate.

6. Other Modifications.

In addition to the modifications discussed above, there have been other modifications in the procedure: Fife, 1959 b; Glenn et al., 1959; Chang and Liaw, 1962; Askinazi, Ginzburg, and Lebedeva, 1963; Fiskell and Spencer, 1964; Chang, Chu, and Erh, 1966; and Peterson and Corey, 1966.

D. Nature and Distribution of Inorganic Phosphorus Forms in Soils

The water soluble plus loosely bound phosphorus consists

of soil solution phosphorus and phosphates of sodium, potassium, ammonium, and magnesium. As far as the aluminum, iron, and calcium-bound forms are concerned, there is a wide range of phosphorus compounds in soils. Aluminum-bound phosphorus may occur as variscite-like, wavellite-like minerals or as precipitated grains on aluminosilicate and gibbsite; whereas, iron-bound phosphorus occurs as strengite-like or dufrenite-like minerals or as precipitated grains on iron oxides. In flooded soils, vivianite, a ferrous phosphate mineral, is usually present. Calcium-bound phosphorus exists in a variety of compounds such as mono, di, and tricalcium phosphates, octacalcium phosphate, a variety of apatite, and as precipitates on calcium carbonate particles.

Occluded phosphorus, as used in this text, consists of the reductant soluble iron-bound phosphorus and the occluded aluminum-iron-bound phosphorus. In the process of chemical weathering, aluminum and iron-bound phosphorus become occluded within iron oxides. Because of the iron oxide coatings, a reduction-chelation treatment is necessary to release this form. This is accomplished by sodium citrate-sodium dithionite - sodium bicarbonate treatment in the fractionation procedure. Bauwin and Tyner (1957a, 1957 b) discussed the nature of occluded phosphorus in detail.

The results of fractionation studies on different soils characteristically show contrasting trends in the distribution of various forms. The distribution of inorganic phosphorus

forms in soils is attributed to several factors such as activities of various ions in soil, pH, age of the soil, drainage, texture, fertilizer practice, mineralogical nature, parent material, climate, topography, activity of soil micro-organisms and plant roots, intensity of chemical weathering, and depth of the soil.

The predominant forms in acid soils are aluminum and iron-bound phosphorus; whereas, alkaline soils contain more calcium-bound phosphorus than other forms. Neutral soils contain varying proportions of these forms. It is observed that, highly weathered soils are rich in aluminum and iron-bound phosphorus and occluded phosphorus. Less weathered soils have more calcium-bound form than other forms. These trends in the distribution of inorganic phosphorus forms suggest that there is a dynamic equilibrium between the forms in soils (Kaila, 1961 b).

E. Application of Fractionation Studies

Presently, the Chang and Jackson procedure receives extensive use in soil genesis and soil fertility investigations. Different workers have utilized the results of inorganic phosphorus fractionation studies as follows:

1. To study the distribution pattern of inorganic phosphorus forms in soils under natural conditions--Chang and Jackson, 1957, 1958; Chu and Chang, 1960; Hamilton and Lessard, 1960; Khin and Leeper, 1960; Wright and Peech, 1960; Askinazi, Ginzburg, and Lebedeva, 1963; John, 1963; Kaila,

1963 b; Soper and Elbagouri, 1964; Bapat et al., 1965; Hanley, 1965; Westin and Buntley, 1966; and Ahmed and Jones, 1967.

2. To study the distribution of inorganic phosphorus forms in soils as related to chemical weathering--Chang and Jackson, 1958; Goel and Agarwal, 1959; Hsu and Jackson, 1960; Dahnke, Malcolm, and Menendez, 1964; Haas, 1964; Floate, 1965; and Hawkins and Kunze, 1965.
3. To study the fate of applied phosphorus in soils--Chai and Caldwell, 1959; Yuan, Robertson, and Neller, 1960; Chang and Chu, 1961; Kaila, 1961 a, 1961 b, 1963 a; Volk and McLean, 1963; Fiskell and Spencer, 1964; Kaila, 1964, 1965 a; Kurtz and Quirk, 1965; Manning and Salomon, 1965; Singh, 1965; and Grigg, 1966.
4. To correlate with plant available forms and develop soil tests--Lavery and McLean, 1961; Hanley, 1962; MacKenzie, 1962; Tyner and Davide, 1962; Chiang, 1963; Susuki, Lawton, and Doll, 1963; Al-Abbas and Barber, 1964 a, 1964 b; Alban, Vacharotayan, and Jackson, 1964; Blanchar and Caldwell, 1964; Jackson, Vacharotayan, and Peterson, 1964; Pratt and Garber, 1964; Savant and Ellis, 1964; Dunbar and Baker, 1965; Grigg, 1965; Kaila, 1965 b; Payne and Hanna 1965; Smith, 1965; Chiang, 1966; Jenkins, 1966; Robertson, Thompson and Hutton, 1966; Sing, Martens, and Obenshain, 1966; and Westin and Buntley, 1966 b.

5. To determine the surface activity of inorganic phosphorus forms in soils--Chang and Chu, 1966.
6. And to study the effect of phosphorus on some physical properties of soils--Lutz et al., 1966.

MATERIALS AND METHODS

A. Soils

Eighteen profiles, three each of five plus one each of three series high in available phosphorus, were taken from virgin sites in 1966. Surface, subsoil, and parent material samples were obtained from each profile. The classification, parent material, horizons sampled, texture of surface soil, and number of profiles of the soil series are given in Table 1. For legal locations of the soil series see Appendices E and F. The soil samples were air dried at room temperature, passed through a 2 mm sieve, and stored in non-sealing screw top containers.

B. Physical Analysis

Mechanical analysis was done on all samples in duplicate by the pipette method as described by Toogood and Peters (1953). The percentages of sand, silt, and clay were based on the oven dry weight of organic matter, carbonate, and soluble salt free material.

C. Chemical Analyses

Inorganic phosphorus fractionation of the soil was carried out according to the Chang and Jackson procedure (1957) as modified by Glenn et al., (1959). The determinations were done in duplicate on all samples except subsoil and parent material samples of Maleb, Beaverhills, Breton, Boundary, and

Table 1. Classification, parent material, horizons, dominant texture, and number of profiles of the soil series

Soil series	Classification	Parent material	Horizons sampled	Texture of surface soil	Number of profiles sampled
Maleb	Orthic Brown	Calcareous till	Ah, Bm, C	Loam	3
Beaverhills	Orthic Black	Calcareous till	Ah, Bm, C	Loam to silt loam	3
Rimbey*	Orthic Dark Grey	Alluvial lacustrine	Ahe, Bt, C	Clay loam	1
Winterburn*	Orthic Dark Grey	Pitted deltaic	Ahe, Bt, C	Silt loam	1
Glory*	Orthic Grey Wooded	Pitted deltaic	Ae, Bt, C	Silty clay loam	1
Breton	Orthic Grey Wooded	Calcareous till	Ae, Bt, C	Loam to fine sandy loam	3
Boundary	Grey Wooded	Acid shale	Ae, Bt, C	Silt loam	3
Heart	Orthic Podzol	Aeolian sand	Ae, Bf, C	Loamy fine sand to fine sand	3

*Series high in available phosphorus.

Table 2. Forms of inorganic phosphorus and the extractants

Form of inorganic phosphorus	Abbreviation	Extractant
Water soluble plus loosely bound*	-	1N NH_4Cl
Aluminum-bound	Al - P	0.5N NH_4F , pH 8.2
Iron-bound	Fe - P	0.1N NaOH
Reductant soluble iron-bound	**	0.3M sodium citrate, sodium dithionite, and 1M NaHCO_3
Occluded aluminum-iron-bound	**	0.1N NaOH
Calcium-bound	Ca-P	0.5N H_2SO_4

* Not determined.

** Occluded phosphorus, as used in this text, stands for reductant soluble iron-bound phosphorus plus occluded aluminum-iron-bound phosphorus.

Heart profiles. The fractionation procedure is discussed in Appendix A-1. The forms of inorganic phosphorus along with the extractants used are given in Table 2.

The extract obtained in the determination of reductant soluble iron-bound phosphorus (Appendix A-1) was used for the estimation of free iron oxides in soils. The iron concentration was determined on a Perkin Elmer Model 303 Atomic Absorption Spectrophotometer.

Determination of pH was done on soil paste (Doughty, 1941) as well as in 0.01 M CaCl_2 (Jackson, 1958). All readings were recorded on a Beckman Zeromatic pH meter equipped with glass and calomel electrodes. The CaCO_3 equivalent was determined gravimetrically by heating the soil with 2N H_2SO_4 containing 5% FeSO_4 and trapping the evolved CO_2 in a weighed Nesbitt bulb filled with alternate layers of Indicarb.

An $\text{HCl-HNO}_3\text{-HF}$ wet oxidation* was followed for the extraction of total phosphorus, iron, aluminum, and calcium. Total analysis was done on all samples in duplicate. The procedure is described in Appendix A-2. Phosphorus was determined by the ascorbic acid-reduced molybdophosphoric blue color method in H_2SO_4 system (Watanabe and Olsen, 1965) as outlined in Appendix A-3. Total iron, aluminum, and calcium were determined on a Perkin Elmer Model 303 Atomic Absorption Spectrophotometer.

* Personal communication with Dr. S. Pawluk, Associate Professor of Soil Science, Univ. of Alberta, Edmonton.

Available phosphorus was extracted by the Miller and Axley ($0.03N \text{ NH}_4\text{F} + 0.03N \text{ H}_2\text{SO}_4$), and Olsen ($0.5M \text{ NaHCO}_3$) methods as outlined by Robertson (1962), except that the ascorbic acid-reduced molybdophosphoric blue color method in H_2SO_4 system was used for the colorimetric determination of phosphorus (see Appendix A-3).

D. Statistical Analyses

Standard deviations and simple correlation coefficients were calculated according to standard methods (Steel and Torrie, 1960).

RESULTS AND DISCUSSION

The detailed results of the various analyses on individual soil samples are given in Appendices C and D. The average concentration of phosphorus forms in the three horizons of the various soil series are reported in Tables 3 and 4. Tables 5 and 6 show the distribution of inorganic phosphorus forms expressed as percent of total inorganic phosphorus and the distribution of Ca-P, Al-P, and Fe-P as percent of active phosphorus*. The percentage distribution of Ca-P, Al-P, Fe-P, occluded phosphorus (Occl-P) and residual plus organic phosphorus (Res+org-P) are shown in Fig. 1 to 4. These tables and figures have been presented to fit roughly the concept that as weathering increases, there is a shift in relative abundance of inorganic phosphorus forms from Ca-P toward Al-P, Fe-P, and Occl-P (Chang and Jackson, 1958).

A. Distribution of Inorganic Phosphorus Forms in the Soil Series

1. Calcium-bound Phosphorus

Ca-P ranges from 1 to 442 ppm (Tables 3 and 4). The highest values (100-400 ppm) are found in the soil series and soil horizons which are least weathered. The very low values (< 15 ppm) occur in the Boundary (derived from acid shale parent material) and in the strongly weathered Ae horizon of the Heart series. Ca-P is the predominant form in the Maleb, Beaverhills and the C

* Active phosphorus = Ca-P + Al-P + Fe-P.

Table 3. Average concentration (ppm) of phosphorus forms in the Chernozemic soil series

Horizon	Ca-P	Al-P	Fe-P	Active P ^a	Occl-P	Total [#] forms	Total P	Res + org-P	Olsen P	Miller & Axley P
<u>MALEB*</u>										
Ah	157	14	21	192	60	252	459	207	6	11
Bm	136	17	16	169	39	208	395	187	3	4
C	314	21	6	341	38	379	423	44	4	1
<u>BEAVERHILLS*</u>										
Ah	88	13	23	124	76	200	810	610	7	4
Bm	117	5	25	147	40	187	350	163	1	1
C	274	6	3	283	16	299	405	106	1	trace
<u>RIMBEY**</u>										
Ahe	69	99	172	340	174	514	930	416	18	67
Bt	76	2	42	120	117	237	385	148	1	3
C	63	11	57	131	157	288	342	54	1	4
<u>WINTERBURN**</u>										
Ahe	68	99	151	318	136	454	738	284	10	60
Bt	108	27	113	248	140	388	600	212	5	18
C	171	6	42	219	106	325	415	90	2	3

* Average of three profiles.

** Single profile.

a Active P = Ca-P + Al-P + Fe-P.

Total forms = Ca-P + Al-P + Fe-P + Occl-P.

Table 4. Average concentration (ppm) of phosphorus forms in the Podzolic soil series

Horizon	Ca-P	Al-P	Fe-P	Active P	Occl-P	Total forms	Total P	Res + org-P	Olsen P	Miller & Axley P
<u>GLORY**</u>										
Ae	42	65	144	251	148	399	662	263	12	47
Bt	110	17	107	234	157	391	500	109	4	8
C	442	6	6	454	54	508	662	154	1	1
<u>BRETON*</u>										
Ae	38	24	55	117	60	177	267	90	6	17
Bt	89	3	31	123	43	166	253	87	1	2
C	295	11	18	324	37	361	468	107	2	2
<u>BOUNDARY*</u>										
Ae	13	19	96	128	104	231	395	164	4	11
Bt	5	5	114	124	98	222	417	195	trace	3
C	7	6	194	207	131	338	488	150	trace	2
<u>HEART*</u>										
Ae	1	6	5	12	1	13	18	5	2	3
Bf	35	398	260	693	143	836	883	47	21	53
C	71	27	82	180	112	292	306	14	10	19

* Average of three profiles.

** Single profile.

Table 5. Average distribution of inorganic phosphorus forms
in the Chernozemic soil series

Horizon	Ca-P --% of total	Al-P --% of total	Fe-P --% of total	Occl-P --% of total inorganic P--	Ca-P --% of active P---	Al-P --% of active P---	Fe-P --% of active P---
<u>MALEB</u>							
Ah	62	6	8	24	82	7	11
Bm	65	8	8	19	80	10	10
C	83	5	2	10	92	6	2
<u>BEAVERHILLS</u>							
Ah	44	6	12	38	72	10	18
Bm	63	3	13	21	79	4	17
C	92	2	1	5	97	2	1
<u>RIMBEY</u>							
Ahe	13	19	34	34	20	29	51
Bt	32	1	18	49	63	2	35
C	22	4	20	54	48	8	44
<u>WINTERBURN</u>							
Ahe	15	22	33	30	21	31	48
Bt	28	7	29	36	43	11	46
C	53	2	13	32	78	3	19

Table 6. Average distribution of inorganic phosphorus forms in the Podzolic soil series

Horizon	Ca-P --% of total	Al-P --% of total	Fe-P --% of total	Occl-P --% of total	Ca-P --% of active	Al-P --% of active	Fe-P --% of active
<u>GLORY</u>							
Ae	10	16	36	38	17	26	57
Bt	28	4	27	41	47	7	46
C	87	1	1	11	98	1	1
<u>BRETON</u>							
Ae	22	14	31	33	39	15	46
Bt	54	2	19	25	74	2	24
C	82	3	5	10	90	4	6
<u>BOUNDARY</u>							
Ae	6	8	41	45	10	14	76
Bt	2	2	52	44	4	4	92
C	2	2	57	39	3	3	94
<u>HEART</u>							
Ae	8	46	38	8	11	47	42
Bf	4	48	31	17	7	53	40
C	24	9	28	39	42	14	44

horizons of Glory and Breton profiles, and this may be explained by the high calcium saturation of their exchange complexes. The high acidity of Boundary profile precludes the presence of Ca-P and this is evident from the very low concentration of this form. With the exception of Boundary, Ca-P concentration increases with depth. The discrepancy observed in the Rimbey may be attributed to insufficient sampling depth.

When expressed as percent of the total inorganic phosphorus (Tables 5 and 6) Ca-P ranges from 10 to 92% in the Maleb, Beaverhills, Glory, and Breton series and from 2 to 53% in the other series. Ca-P constitutes 82 to 92% of the inorganic phosphorus in the C horizons of the first group of soils. What is more evident is the low content of Ca-P in Boundary, where it is only 2 to 6% of the inorganic phosphorus.

2. Aluminum-bound Phosphorus

Al-P varies from 2 ppm in the Bt of Rimbey to 398 ppm in the Bf of Heart series (Tables 3 and 4). There is a tendency for Al-P to decrease with depth in all the series except Heart, where it shows a marked accumulation in the Bf horizon. This accumulation in the Bf of Heart series may be attributed to increased weathering of the Ae horizon resulting in the dissolution of aluminum and phosphorus containing compounds and subsequent precipitation. The three series high in available phosphorus (Rimbey, Winterburn and Glory) have characteristically higher amounts of Al-P in their surface horizons.

When expressed as percent of the total inorganic phosphorus, Al-P varies from 1 to 48% (Tables 5 and 6). If the Heart series is excluded, the percent of Al-P is comparatively low and with the exception of surface horizons, its content is relatively constant. Such a trend supports the suggestion of Chang and Jackson (1958) that it is a transition phase in the weathering sequence Ca-P--Al-P--Fe-P--Occl-P.

3. Iron-bound Phosphorus

Fe-P varies from 5 to 260 ppm (Tables 3 and 4). Fe-P concentration decreases with depth in all the soils except Boundary and Heart series. In the Boundary Fe-P increases with depth and it is the predominant form. In Heart the Ae horizon is leached of this form and there is an accumulation in the Bf horizon. Fe-P occurs in higher concentrations in the Rimbey, Winterburn and Glory series.

When expressed as percent of the total inorganic phosphorus, Fe-P varies from 1 to 57% (Tables 5 and 6). The higher percentages (> 30) occur in the surface horizons of Rimbey, Winterburn, Glory, Breton, Heart, and throughout the Boundary profiles.

4. Occluded Phosphorus

Occl-P varies from 1 to 174 ppm (Tables 3 and 4). Occl-P content decreases with depth in the Maleb, Beaverhills, and Breton series. The Rimbey, Winterburn, and Glory (high in available phosphorus) are comparatively high in this form, as are the Boundary and Heart series. The high amount of Occl-P in the A

and B horizons compared to the C horizons suggests that its accumulation is related to weathering and soil development processes. Weathering processes increase the activity and mobility of iron. Occl-P concentration is less in soils developed under calcification than in the case where acid leaching and iron movement occur as in podzolization (Allaway and Rhoades, 1951).

Occl-P content ranges from 5 to 54% of the total inorganic phosphorus (Tables 5 and 6). According to Chang and Jackson (1958), this is the most resistant of the inorganic forms. One might, therefore, expect to find a higher content of Occl-P in the Heart series than in the others. The discrepancy observed in the distribution of this form in the Heart series may be due to low clay content. The acid parent material of the Boundary series may account for the differences between the concentration of Occl-P in this soil and the Breton series.

B. Relationship between Physical and Chemical Properties and the Distribution of Inorganic Phosphorus Forms

The particle size analysis data are reported in Appendix B. There is no apparent relationship between the distribution of soil separates and inorganic phosphorus forms.

The results of chemical analyses are given in Tables 7 and 8. Although soil reaction is not closely correlated with Al-P, Fe-P, and Occl-P contents, which agrees with the report of Tandon et al., (1967), the results show two general trends.

First, acid soils are high in Al-P, Fe-P, and Occl-P; secondly alkaline soils are high in Ca-P. Sometimes, even in acid or alkaline soils, varying proportions of Ca-P, Al-P, and Fe-P occur and such distribution patterns may be because of random pockets of alkalinity and acidity (Chang and Jackson, 1958).

The results for Fe-P and free Fe_2O_3 do not suggest any relationship between the two. But, there is a relationship between Ca-P contents and CaCO_3 equivalent in the soils developed on calcareous parent materials (Maleb, Beaverhills, Glory, Breton). Above pH 7 Ca-P is more stable than Al-P and Fe-P in soils, particularly in the presence of CaCO_3 (Hsu and Jackson, 1960). Further, there seems to be a general relationship between the Ca-P and total calcium contents in the soils and this agrees with the observation of Ahmed and Jones (1967). However, there is no apparent relationship between the contents of total aluminum and iron and concentration of Al-P and Fe-P in the soils. This may be because of the manyfold concentration of Al and Fe ions compared to phosphate ion in soils.

C. Effect of Parent Material and Climate on the Distribution of Inorganic Phosphorus Forms

Table 9 shows the average distribution of phosphorus forms in the C horizons of soil series formed on various parent materials. Ca-P accounts for 63 to 74% (mean 68%) of the total phosphorus in the C horizons of soils developed on till. The acid shale and aeolian sand parent materials are rich in Fe-P

Table 7. Average chemical properties of the Chernozemic soil series

Horizon	pH in soil paste	pH in 0.01M CaCl ₂	Free Fe ₂ O ₃ %	CaCO ₃ equi- valent %	Fe ₂ O ₃ %	Al ₂ O ₃ %	CaO %
<u>MALEB</u>							
Ah	7.0	6.7	.62	.11	2.94	9.20	1.10
Bm	7.1	6.9	.88	.04	3.69	10.64	1.11
C	8.0	7.9	.83	3.41	2.92	10.11	2.37
<u>BEAVERHILLS</u>							
Ah	6.2	5.9	1.05	.09	2.73	10.96	1.28
Bm	6.3	6.1	1.23	.08	3.79	12.76	.93
C	7.6	7.5	.93	3.63	3.13	10.49	2.69
<u>RIMBEY</u>							
Ahe	5.8	5.4	.93	.21	2.63	7.24	1.10
Bt	6.1	5.9	1.14	.08	3.60	8.41	.79
C	6.1	5.9	1.14	trace	3.60	10.58	.76
<u>WINTERBURN</u>							
Ahe	5.8	5.5	.93	.12	3.14	11.15	.82
Bt	5.4	5.3	1.33	.01	4.76	13.89	.85
C	5.3	5.1	1.10	trace	4.38	13.42	.94

Table 8. Average chemical properties of the Podzolic soil series

Horizon	pH in soil paste	pH in 0.01M CaCl ₂	Free Fe ₂ O ₃ %	CaCO ₃ equi- valent %	Fe ₂ O ₃ %	Al ₂ O ₃ %	CaO %
<u>GLORY</u>							
Ae	6.5	6.2	1.00	.10	3.50	9.45	.76
Bt	4.9	4.7	2.46	.03	5.62	10.58	.81
C	7.5	7.4	1.87	3.02	5.04	9.86	2.52
<u>BRETON</u>							
Ae	5.2	4.7	.75	.11	2.31	8.82	.63
Bt	4.6	4.5	1.19	.03	3.38	12.09	.78
C	6.8	6.7	1.11	1.42	3.19	11.34	1.72
<u>BOUNDARY</u>							
Ae	4.7	4.1	1.11	.08	2.63	8.21	.33
Bt	4.4	3.9	1.51	.06	4.03	12.67	.28
C	4.2	3.7	1.59	.07	5.19	14.84	.21
<u>HEART</u>							
Ae	4.2	3.7	.16	trace	.33	2.90	.18
Bf	5.5	4.8	.91	.12	1.56	3.92	.22
C	5.5	4.9	.87	.01	2.09	5.42	.31

and Occl-P. Note also the prominence of Ca-P in aeolian sand. However, it is not possible to draw any conclusion concerning the distribution of inorganic phosphorus forms in the pitted deltaic and alluvial lacustrine parent materials because of the limited number of profiles and insufficient sampling depths in two of them.

Generally, with degree development, the content of Ca-P, which is the least resistant among the four forms of inorganic phosphorus, decreases in soils. The effect of climate, as expressed through the Great Groups, is sometimes nullified by the influence of parent materials. This is evident from the higher amount of Ca-P in the C horizon of Breton than that of Boundary series (Tables 3 and 4), and different inorganic phosphorus distribution patterns in the Glory, Breton, and Boundary series--all belonging to the Grey wooded Great Group (Tables 5 and 6). Glory and Breton soils have most of the inorganic phosphorus as Ca-P in the C horizons, whereas Fe-P and Occl-P are the predominant forms in the Boundary C horizon.

The soils are arranged in Fig. 1 to 4 in increasing order of weathering. The weathering sequence, based on the distribution of inorganic phosphorus forms, proposed by Chang and Jackson (1958), holds good only in the case of soils formed on the same parent materials. Some of the discrepancies observed in the above soils may be attributed to the variety of parent materials.

Table 9. Average distribution of phosphorus forms in the C horizons of soil series formed on various parent materials

Parent material	Ca-P -----	Al-P -----	Fe-P -----	Occl-P % of total P	Res + org - P -----	Total P ppm
Till*	68	3	2	7	20	432
Pitted deltaic**	54	1	6	17	22	538
Alluvial lacustrine	18	3	17	46	16	342
Acid shale	1	1	39	27	32	488
Aeolian sand	27	8	26	33	6	306

* Average of 3 profiles each of Maleb, Beaverhills, and Breton series.

** Average of 1 profile each of Winterburn and Glory series.

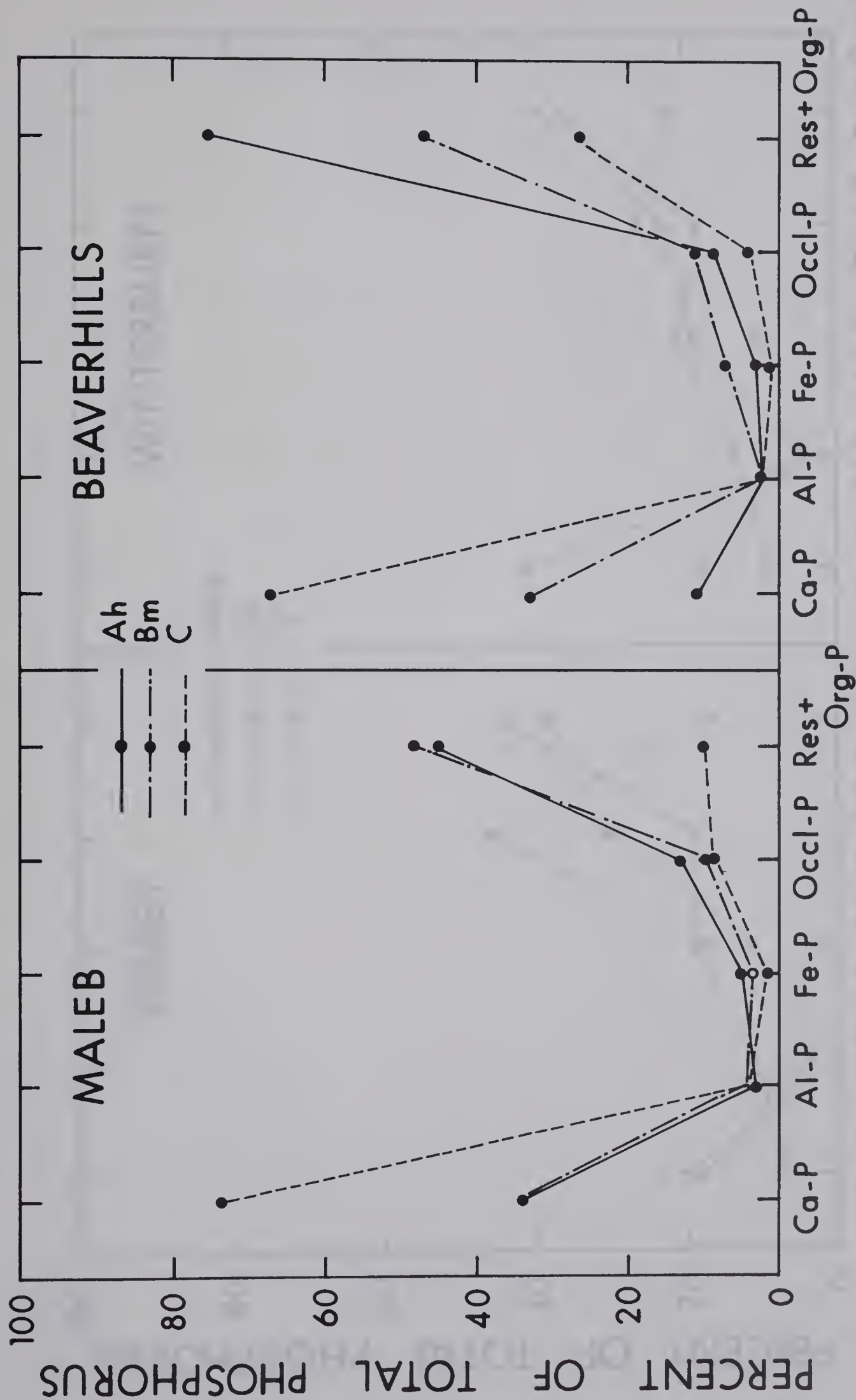
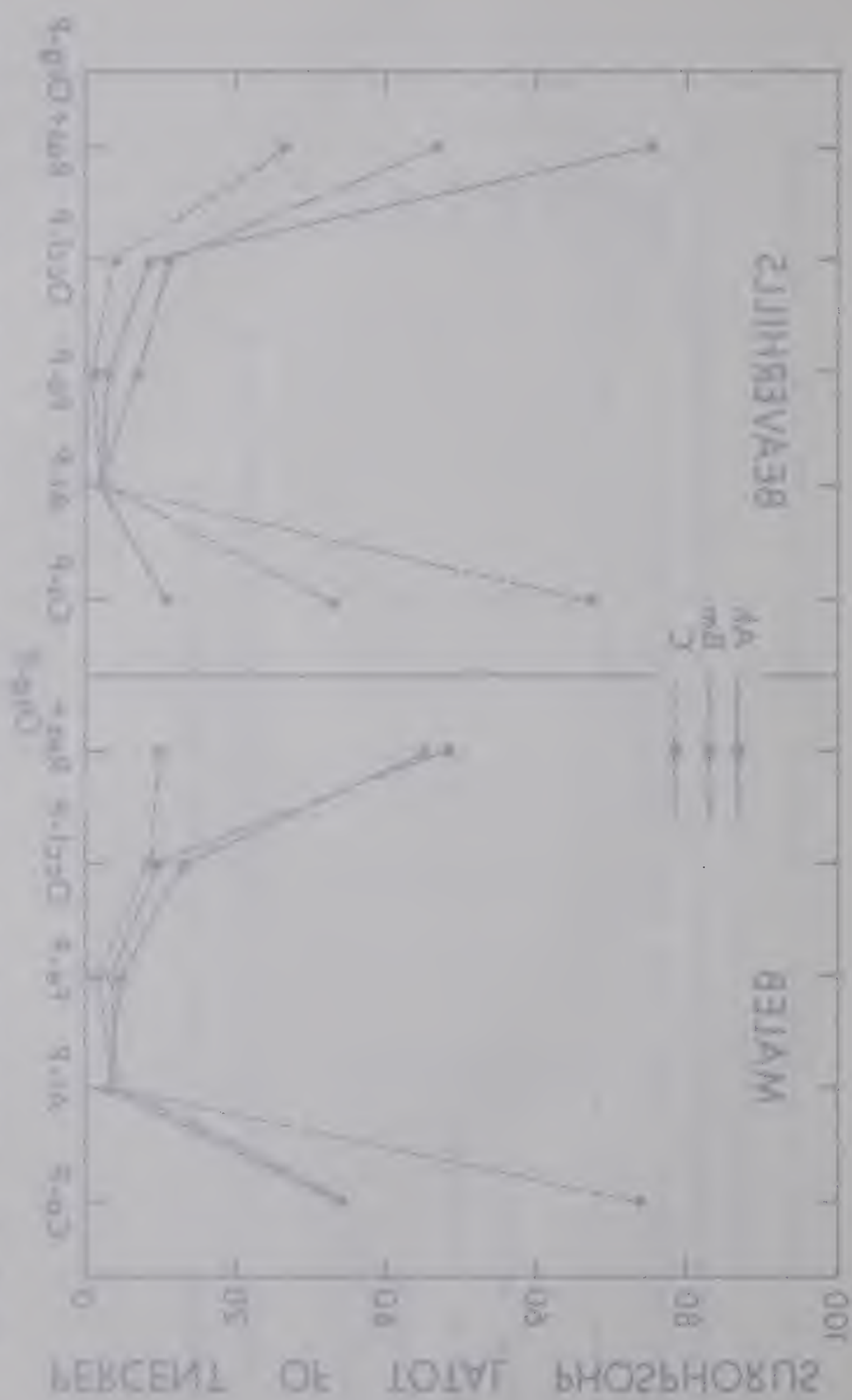


FIG. 1 PERCENTAGE DISTRIBUTION OF PHOSPHORUS FORMS IN THE MALEB AND BEAVERHILLS SERIES

FIG. 1. PERCENTAGE DISTRIBUTION OF PHOSPHORUS IN THE WATER AND BEVERKINTZ SERIES



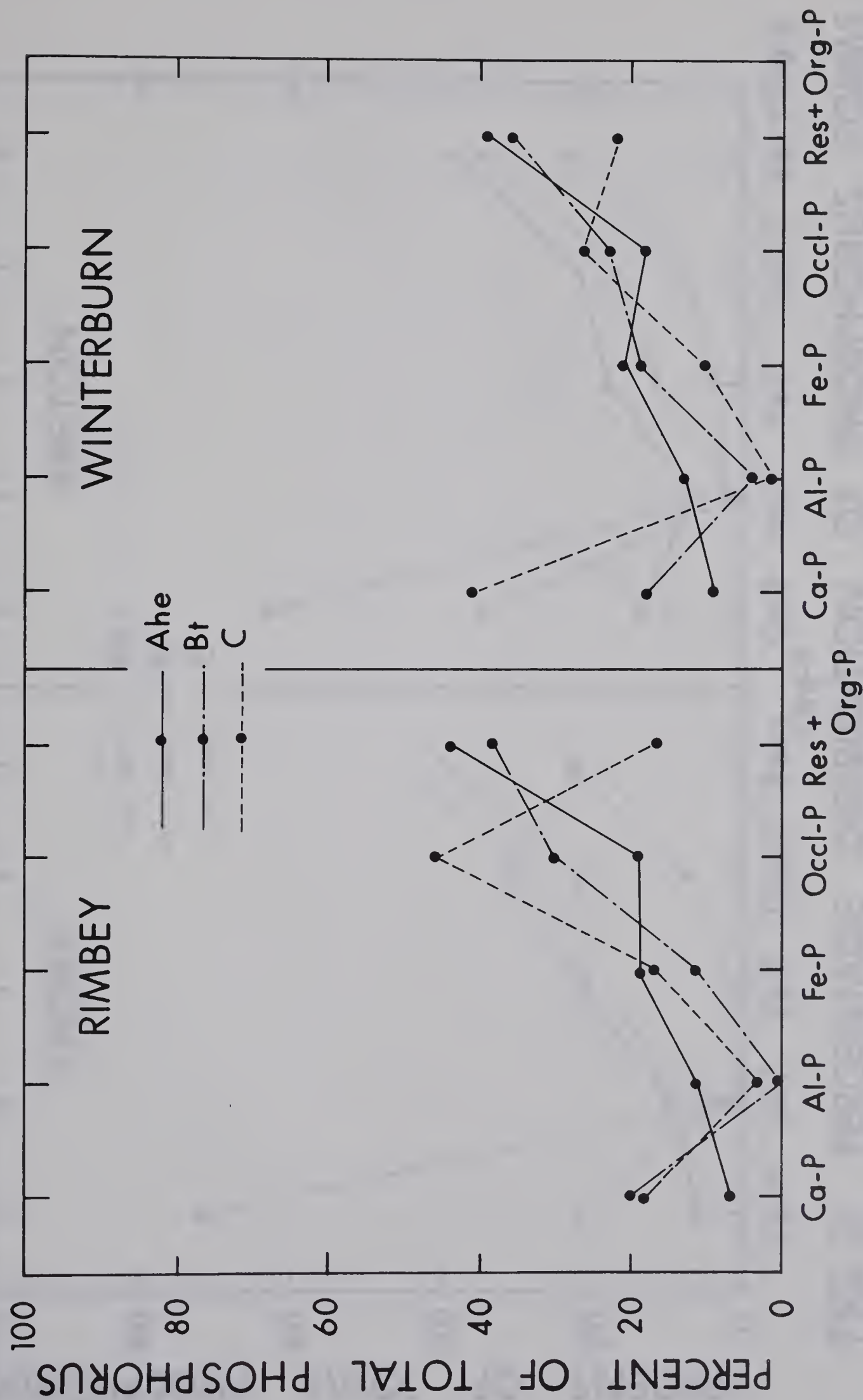


FIG. 2 PERCENTAGE DISTRIBUTION OF PHOSPHORUS FORMS IN THE RIMBEY AND WINTERBURN SERIES

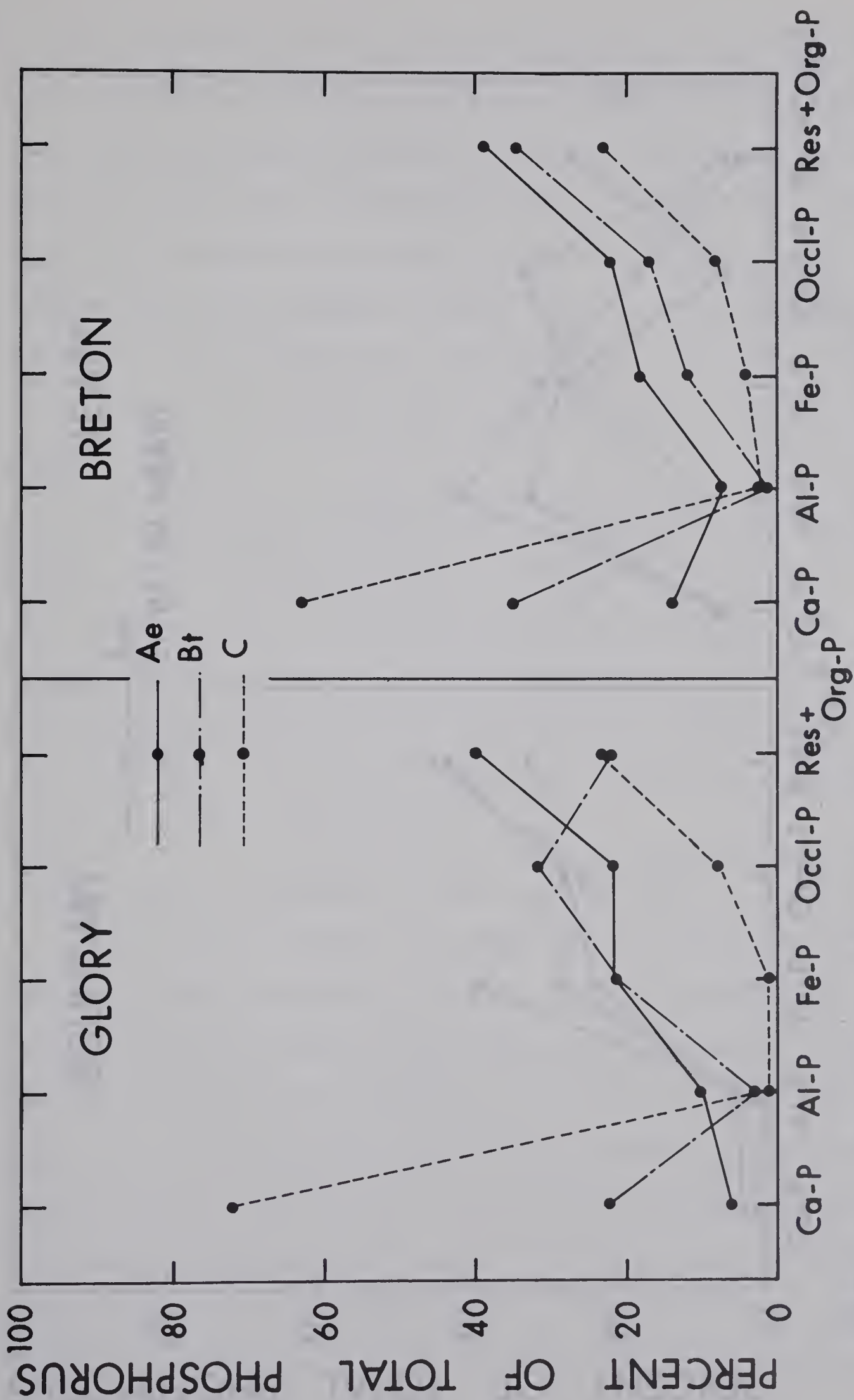


FIG. 3 PERCENTAGE DISTRIBUTION OF PHOSPHORUS FORMS IN THE GLORY AND BRETON SERIES

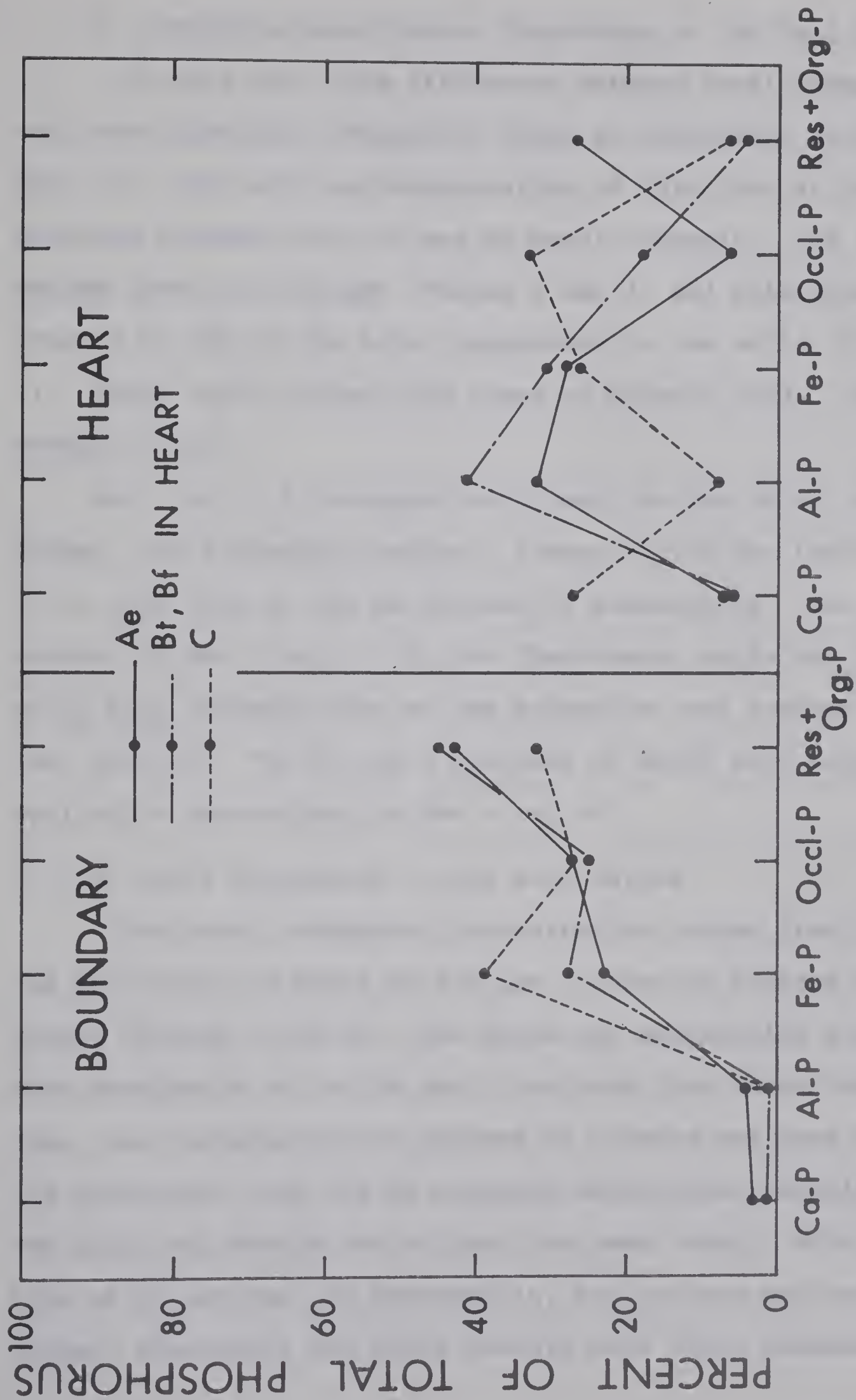


FIG. 4 PERCENTAGE DISTRIBUTION OF PHOSPHORUS FORMS IN THE BOUNDARY AND HEART SERIES

D. Residual plus Organic Phosphorus in the Soil Series

In this text, the difference between total phosphorus and total inorganic phosphorus forms is considered as Res + org - P. The very low concentration of this form in some horizons suggests that it may be mostly organic. Res + org - P varies from 5 to 610 ppm (Tables 3 and 4) and this form constitutes 4 to 75% of the total phosphorus in the soils (Fig. 1 to 4). These values agree with those of Odymsky (1934, 1936) and Dormaar (1961).

Res + org - P decreases with depth in the Maleb, Beaverhills, Rimbey, and Winterburn series. Almost 75% of the total phosphorus is in this form in the Ah horizon of Beaverhills. The high amounts of Res + org - P in the Chernozemic soils may be because of in situ decomposition of the extensive root systems of grassland species. The Bf and C horizons of Heart soil have only negligible percentages as Res + org -P.

E. Total Phosphorus in the Soil Series

The total phosphorus concentration ranges from 18 ppm in the Ae horizon of Heart to 930 ppm in the Ahe horizon of Rimbey series (Tables 3 and 4). The Maleb and Beaverhills soils have more phosphorus in the Ah and C horizons than in the Bm horizons. Here, more extensive root systems of grasses may have depleted the phosphorus from the Bm horizons during their development. The Glory and Breton series have the same trend. With the exception of Ah horizon of Beaverhills, the surface horizons of Rimbey, Winterburn and Glory contain more total phosphorus than

do the surface horizons of the other series. One might expect this trend from the higher amount of inorganic phosphorus forms in these soils. In the Rimbey and Winterburn series phosphorus decreases with depth; and in Boundary it increases with depth. There is an accumulation of phosphorus in the Bf horizon of Heart series.

F. Available Phosphorus in the Soil Series

One of the immediate applications of inorganic phosphorus fractionation studies is to understand the nature of plant available phosphorus in soils. Available phosphorus was determined by the Miller and Axley, and Olsen methods. Fig. 5 to 7 are presented to show the relationship between available phosphorus and the active forms (Ca-P, Al-P, Fe-P). Only the surface horizon values are considered for correlation. Except in the case of the Rimbey, Winterburn, and Glory series, where only one profile of each was studied, average values are plotted.

The Rimbey, Winterburn, and Glory soils show high amounts of available phosphorus by both methods and by barley yields in field experiments.* Note that the surface horizons of these soils are characteristically high in active forms, especially Al-P and Fe-P (Tables 3 and 4). Although the Bf horizon of Heart series is considerably higher in active forms, the available phosphorus concentration is not much different

*Unpublished data. Department of Soil Science, Univ. of Alberta, Edmonton.

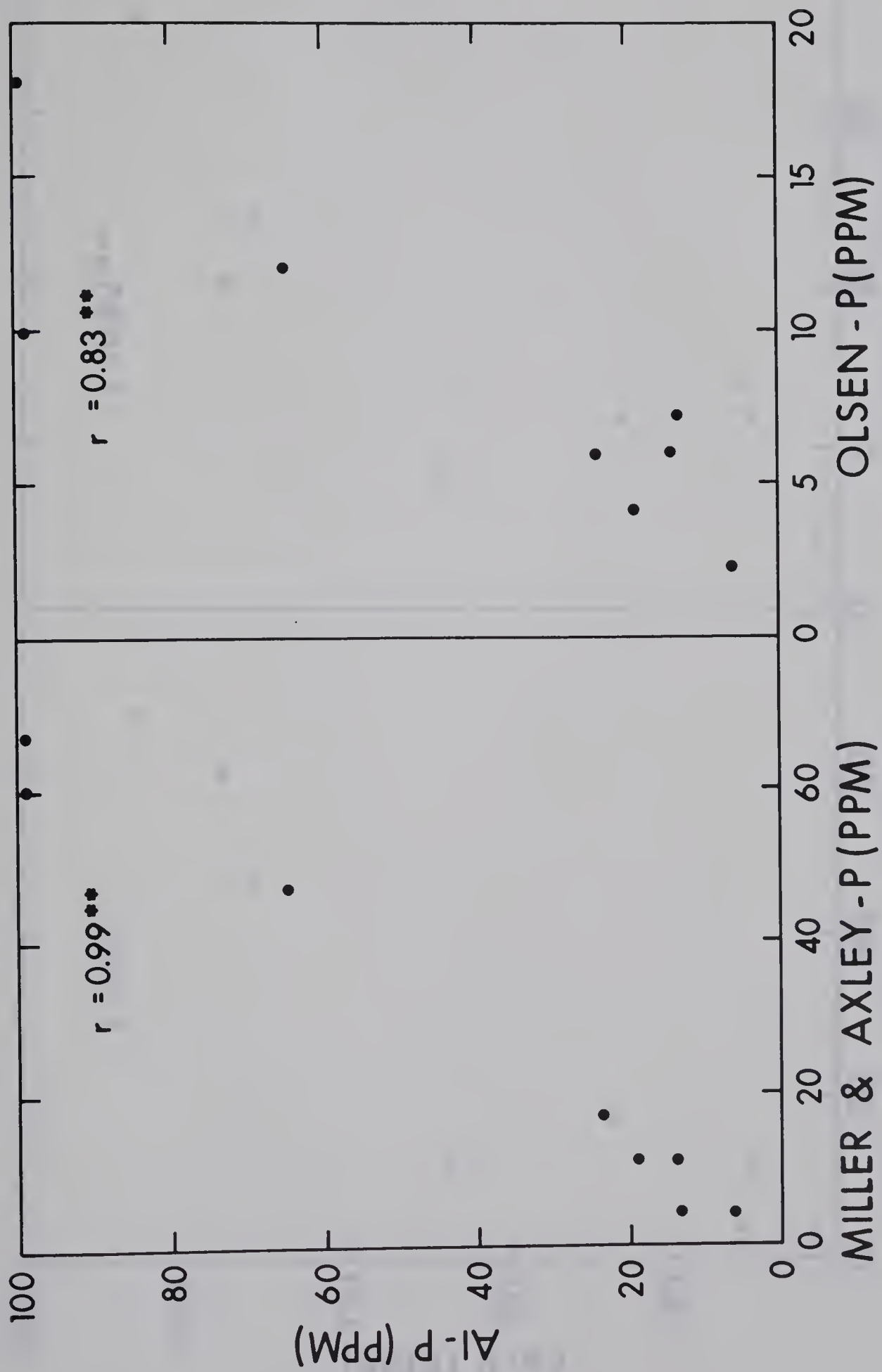


FIG. 5 RELATIONSHIP BETWEEN AVAILABLE PHOSPHORUS AND AL-P

** SIGNIFICANT AT THE 1% LEVEL

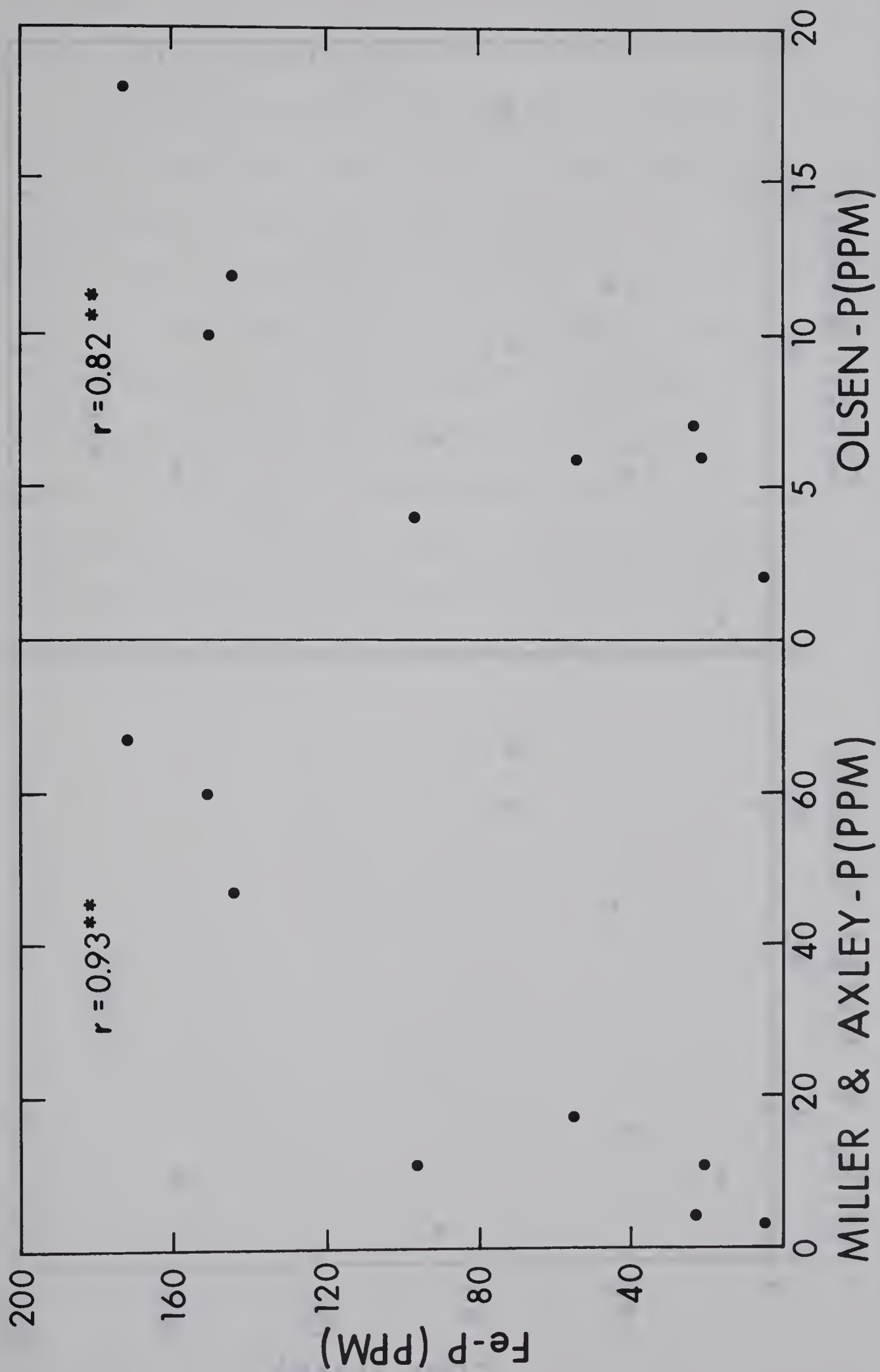


FIG. 6 RELATIONSHIP BETWEEN AVAILABLE PHOSPHORUS AND Fe-P

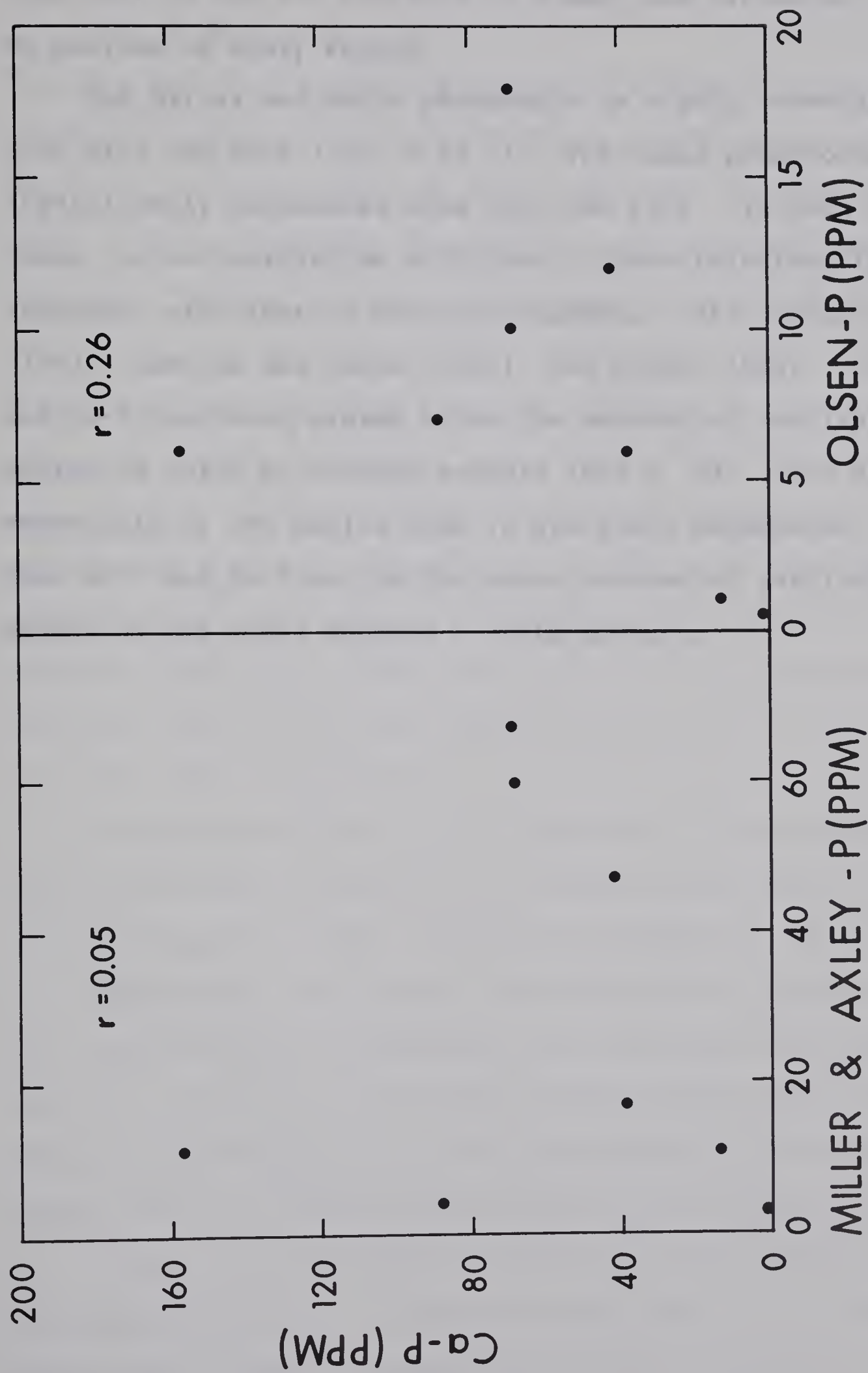


FIG. 7 RELATIONSHIP BETWEEN AVAILABLE PHOSPHORUS AND Ca-P

from that of the Ahe horizons of Rimbey and Winterburn and Ae horizon of Glory series.

The Miller and Axley phosphorus is highly correlated with Al-P and Fe-P (Fig. 5 to 7). The Olsen phosphorus is significantly correlated with Al-P and Fe-P. In both cases, there is no correlation with Ca-P. These relationships are in agreement with that of Chai and Caldwell (1959), Susuki et al. (1963), Hawkins and Kunze (1965), and Grigg (1966). Al-P, Fe-P, and Ca-P have been proved to be the sources of available phosphorus in soils by various workers (see p. 14). The data, especially of the series high in available phosphorus, indicate that Al-P and Fe-P may be the major sources of available phosphorus in the soils studied in this project.

SUMMARY AND CONCLUSIONS

An investigation was carried out to study the amount and distribution of inorganic phosphorus forms in eighteen profiles of Alberta soils, three each of Maleb, Beaverhills, Breton, Boundary, and Heart plus one each of Rimbey, Winterburn, and Glory (high in available phosphorus). Surface, (Ah, Ahe, Ae horizons), subsoil (Bm, Bt, Bf horizons), and parent material (C horizon) samples were obtained from each profile. Inorganic phosphorus forms in the soils were fractionated by the modified Chang and Jackson procedure. The forms determined were: calcium-bound (Ca-P), aluminum-bound (Al-P), iron-bound (Fe-P), and occluded (Occl-P) phosphorus. In addition, the following determinations were done on all samples; pH; particle size analysis; free Fe_2O_3 ; CaCO_3 equivalent; total phosphorus, iron, aluminum, and calcium; and available phosphorus by the Miller and Axley, and Olsen methods.

Ca-P ranges from 1 to 442 ppm and it is the predominant form in the Maleb, Beaverhills, and the C horizons of Glory and Breton series. When expressed as percent of the total inorganic phosphorus, Ca-P varies from 10 to 92% in these soils. With the exception of Boundary, Ca-P increases with depth in all the soils. There is close relationship between Ca-P contents and CaCO_3 equivalent in the soils developed on calcareous parent materials (Maleb, Beaverhills, Glory, Breton).

The Al-P concentration varies from 2 to 398 ppm. There is a tendency for Al-P to decrease with depth in all the series except Heart, where it accumulates in the Bf horizon. Al-P

ranges from 1 to 48% of the total inorganic phosphorus.

Fe-P extends from 5 to 260 ppm. Fe-P decreases with depth in all the series except Boundary and Heart. In the Boundary, it increases with depth and in the Heart, there is, as for Al-P, an accumulation in the Bf horizon. When expressed as percent of the total inorganic phosphorus, Fe-P varies from 1 to 57%. The Rimbey, Winterburn, and Glory series (high in available phosphorus) have 3 to 8 times more of Al-P and Fe-P in their surface horizons compared to those of Maleb, Beaverhills and Breton.

Occl-P ranges from 1 to 174 ppm. Generally, Occl-P decreases with depth in the Maleb, Beaverhills and Breton series. With the exception of the Heart Ae horizon, the other soils are comparatively high in this form. It constitutes 5 to 54% of the total inorganic phosphorus.

There is no apparent relationship between the distribution of soil separates and inorganic phosphorus forms. Generally, acid soils are high in Al-P, Fe-P, and Occl-P; while alkaline soils are high in Ca-P. Parent material and climate seem to have an effect on the distribution of inorganic phosphorus forms in the soils. On the basis of genesis, the soils are arranged in the following sequence: Maleb, Beaverhills, Rimbey, Winterburn, Glory, Breton, Boundary, and Heart. Though some discrepancies due to the variety of parent materials are observed, the weathering sequence based on the percentage distribution of inorganic phosphorus forms fits in approximately with the above sequence.

The residual plus organic phosphorus (Res + org-P)--the difference between total phosphorus and total inorganic phosphorus forms--varies from 5 to 610 ppm and it constitutes 4 to 75% of the total phosphorus in the soils. It is thought that most of the phosphorus in this form is in organic combination. Res + org-P decreases with depth in the Chernozemic soils. Almost 75% of the total phosphorus is in this form in the Ah horizon of Beaverhills series. Compared to the Breton and Heart soils, Boundary has more of this form.

The total phosphorus varies from 18 to 930 ppm. The Ah or Ae and C horizons of Maleb, Beaverhills, Glory, and Breton series have more phosphorus than do the Bm or Bt horizons. With the exception of Ah horizon of Beaverhills, the surface horizons of Rimbey, Winterburn, and Glory contain more total phosphorus than do the surface horizons of the other series. In the Rimbey and Winterburn soils, phosphorus decreases with depth, while in Boundary it increases with depth. There is an accumulation of phosphorus in the Bf horizon of Heart series.

Correlation coefficients were calculated for available phosphorus on the surface horizons versus Ca-P, Al-P, and Fe-P. The Miller and Axley phosphorus is highly correlated with Al-P and Fe-P. The Olsen phosphorus is significantly correlated with Al-P and Fe-P. In both cases, there is no correlation with Ca-P. These data indicate that Al-P and Fe-P may be the major sources of available phosphorus in the soils studied.

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APPENDIX A-1. Modified Chang and Jackson Procedure for
Fractionation of Inorganic Soil Phosphorus

a) Special Reagents

Chloromolybdic acid solution-- Dissolve 15 g ammonium molybdate in about 300 ml of water by warming to about 50°C. Filter the solution if cloudy. Cool the solution and add 350 ml of 10N HCl slowly with stirring. Cool the solution again, dilute with water to 1 liter, and store in a brown bottle.

Sulfomolybdic acid solution--Dissolve 25g of ammonium molybdate in 200 ml of water by warming to about 60°C. Filter if cloudy. Dilute 275 ml of arsenic and phosphorus free conc. H_2SO_4 to 800 ml. After both solutions have cooled, add the ammonium molybdate solution to the H_2SO_4 solution with stirring, and make up the solution to 1 liter when cooled.

Chlorostannous reductant A--Dissolve 10 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 ml of conc. HCl. Store in a brown bottle. Dilute 3 ml of this stock solution to 1 liter not longer than 4 hr. before use.

Chlorostannous reductant B--Dissolve 20 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 ml conc. HCl. Store in a brown bottle. Dilute 2 ml of this stock solution to 20 ml just before use.

b) Standard Curves

A separate standard curve should be prepared for each phosphorus fraction. In preparing standard curves for the individual fractions, the standards should be treated exactly

like the samples in the procedure so that the standards contain the same concentrations of extractants or added reagents as the sample solutions.

c) ^cFr_Ationation Procedure

Extraction and determination of aluminum-bound phosphorus

--Place 1 g of ^{air}oven dried soil in a 100-ml polypropylene centrifuge tube, add 50 ml of 1N NH_4Cl , and shake for 30 min. to remove water soluble plus loosely bound phosphorus and exchangeable calcium. Centrifuge the suspension at 1,600 rpm for 15 min and discard the supernatant solution. Add 50 ml of 0.5N NH_4F , adjusted to pH 8.2 by addition of 4N NH_4OH , to the soil and shake for 1 hr. Centrifuge the suspension for 15 min at 1,600 rpm. Phosphorus in the extract is determined by the chlorostannous-reduced molybdophosphoric blue color method in HCl system as outlined by Jackson (1958, p. 162).

Use separate blanks for the correction of organic matter coloration. Dilute the colored extract with all reagents except ammonium molybdate and measure the intensity of color against a blank prepared in the same manner. The ppm of phosphorus thus obtained is subtracted from the actual value.

Extraction and determination of iron-bound phosphorus--

Wash the soil twice with 25 ml portions of saturated NaCl by centrifugation at 1,600 rpm for 10 min. Add 50 ml of 0.1N NaOH and shake for 10 hr. Centrifuge the suspension for 15 min

at 2,400 rpm and decant the supernatant solution into 100 ml polypropylene centrifuge tubes. Add 2 ml of 2N H_2SO_4 and centrifuge to throw down organic matter. Phosphorus in the extract is determined by the chlorostannous-reduced molybdophosphoric blue color method in H_2SO_4 system as described by Jackson (1958, p. 165).

Extraction and determination of reductant soluble iron-bound phosphorus--Wash the soil sample twice with 25 ml portions of saturated NaCl by centrifugation at 1,600 rpm for 10 min. Add 40 ml of 0.3M sodium citrate and 5 ml of 1M NaHCO_3 to the soil and keep the tube at 80-90°C in a water bath for 10 min. Add 1 g of sodium dithionite to the suspension with stirring and keep the tube for another 15 min in the water bath. Centrifuge the suspension for 15 min at 1,600 rpm and collect the supernatant solution in a 100-ml volumetric flask. Wash the soil twice with 25-ml portions of saturated NaCl by centrifugation at 1,600 rpm for 10 min and transfer the supernatant solution to the same flask. Make up to volume and determine phosphorus in the extract by the procedure outlined by Jackson (1958, p. 168-169).

Extraction and determination of occluded aluminum-iron-bound phosphorus--Add 50 ml of 0.1N NaOH to the soil and shake for 10 hr. Centrifuge the suspension for 15 min at 2,400 rpm. Phosphorus in the extract is determined by the chlorostannous-reduced molybdophosphoric blue color method in H_2SO_4 system as described by Jackson (1958, p. 165).

Extraction and determination of calcium-bound phosphorus--

Wash the soil twice with 25-ml portions of saturated NaCl by centrifugation at 1,600 rpm for 10 min. Add 50 ml of 0.5N H_2SO_4 and shake for 1 hr. Centrifuge the suspension for 15 min at 1,600 rpm. Phosphorus in the extract is determined by the Chlorostannous-reduced molybdophosphoric blue color method in H_2SO_4 system outlined by Jackson (1958, p. 157).

Appendix A-2. Determination of Total Soil Phosphorus

Weigh 1 g of oven dried soil into a porcelain crucible and ignite in a muffle furnace at 500°C for 1 hr. Transfer the ignited sample to a 100-ml teflon beaker with 1+1 HCl. Evaporate to about 10 ml. Add 15 to 20 ml conc. HCl to the beaker and evaporate to dryness. Add 10 ml of conc. HNO_3 and 10 ml of 48% HF to the beaker and again evaporate to dryness. This step is repeated. Dissolve the residue with 10 ml of conc. HCl and 30 ml of water. Transfer the solution to a 200-ml volumetric flask. To the beaker add a few ml of 1+1 HCl and place back on the sand bath to remove the residue. Transfer the solution to the same flask and solution is made up to volume with 5% HCl. A blank extract is prepared in the same way with all the reagents except soil. Phosphorus in the extract is determined by the ascorbic acid-reduced molybdophosphoric blue color method in H_2SO_4 system as described in Appendix A-3.

Appendix A-3. Ascorbic Acid-Reduced Molybdophosphoric Blue
Color Method, in H_2SO_4 System

a) Reagents

Reagent A-- Dissolve 12 g of ammonium molybdate in 250 ml of water. In 100 ml of water dissolve 0.2908 g of antimony potassium tartarate. Add both of the dissolved reagents to 1 liter of 5N H_2SO_4 , mix thoroughly and make to 2 liter. Store in pyrex glass bottle in a dark and cool compartment.

Reagent B--Dissolve 1.056 g of ascorbic acid in 200 ml of reagent A. Prepare this reagent as required as it does not keep for more than 24 hr.

b) Determination of Phosphorus

Pipette aliquots containing 1 to 20 ug (0.08 to .80 ppm P in final volume) of orthophosphate into 25-ml volumetric flasks. Adjust to pH 5 using P-nitrophenol indicator. Pre-determine the amount of acid or alkali needed to bring pH to 5 in some aliquots and dispense the same amount to all unknowns. Add water to 20 ml and then add 4 ml of reagent B and the solution is made to volume. The color is stable for 24 hr. and maximum intensity is obtained in 10 min. The color intensity is read on a spectrophotometer at 882 mu. The reduced heteropoly molybdophosphoric acid has two light maxima, one in the vicinity of 690 mu and the other at 882 mu.

Appendix B. Particle size analysis

Profile Number	Horizon	Depth in inches	Sand %	Silt %	Clay %	Class
<u>MALEB</u>						
1	Ah	0 - 3	45	39	16	L
	Bm	3 - 12	41	28	31	CL
	C	30 - 42	42	32	26	L
2	Ah	0 - 3	37	47	16	L
	Bm	3 - 14	39	30	31	CL
	C	30 - 36	40	37	23	L
3	Ah	0 - 2	42	42	16	L
	Bm	2 - 8	41	27	32	CL
	C	24 - 34	40	36	24	L
<u>BEAVERHILLS</u>						
1	Ah	0 - 21	35	39	26	L
	Bm	26 - 33	42	34	24	L
	C	36+	39	37	24	L
2	Ah	0 - 12	24	50	26	SiL
	Bm	18 - 30	15	53	32	SiCL
	C	35+	41	37	22	L
3	Ah	0 - 17	26	48	26	SiL
	Bm	24 - 40	12	58	30	SiCL
	C	40+	41	39	20	L
<u>RIMBEY</u>						
-	Ahe	2 - 15	28	43	29	CL
	Bt	15 - 27	27	51	22	SiL
	C	27+	22	56	22	SiL
<u>WINTERBURN</u>						
-	Ahe	2 - 8	17	60	23	SiL
	Bt	8 - 16	8	60	32	SiCL
	C	16+	22	49	29	CL
<u>GLORY</u>						
-	Ae	1 - 4	3	62	35	SiCL
	Bt	12 - 28	2	68	30	SiCL
	C	28+	1	79	20	SiL

Appendix B. (continued)

Profile Number	Horizon	Depth in Inches	Sand %	Silt %	Clay %	Class
<u>BRETON</u>						
1	Ae	3 - 8	55	37	8	FSL
	Bt	12 - 25	48	24	28	FSCL
	C	36+	48	31	21	L
2	Ae	2 - 6	49	37	14	L
	Bt	9 - 23	32	20	48	C
	C	23+	40	31	29	CL
3	Ae	2 - 6	46	44	10	VFSL
	Bt	9 - 32	40	25	35	CL
	C	32+	40	34	26	L
<u>BOUNDARY</u>						
1	Ae	1 1/2 - 4 1/2	23	56	21	SiL
	Bt	7 1/2 - 11 1/2	14	54	32	SiCL
	C	16 1/2 - 21 1/2	8	32	60	C
2	Ae	1 1/2 - 4 1/2	20	53	27	SiL
	Bt	6 1/2 - 9 1/2	16	58	26	SiL
	C	11 1/2 - 14 1/2	10	42	48	SiC
3	Ae	1 1/2 - 4	16	59	25	SiL
	Bt	7 - 11	8	54	38	SiCL
	C	15+	10	40	50	SiC
<u>HEART</u>						
1	Ae	1 - 2	81	15	4	LFS
	Bf	2 - 8	87	11	2	FS
	C	14+	58	20	22	VFSL
2	Ae	1 - 3	87	9	4	FS
	Bf	3 - 9	88	12	trace	FS
	C	15+	92	trace	8	FS
3	Ae	1 - 3	86	9	5	FS
	Bf	3 - 6	79	21	trace	LFS
	C	9+	87	3	10	LFS

Appendix C-1. Concentration (ppm) of phosphorus forms in the Maleb series

Horizon	Ca-P	Al-P	Fe-P	Occl-P	Total forms	Total P	Residual+ organic P	Olsen P	Miller & Axley P
<u>Profile_1</u>									
Ah	136	22	31	64	253	455	202	10	20
Bm	113	12	23	36	184	395	211	6	9
C	312	7	5	33	357	415	58	5	1
<u>Profile_2</u>									
Ah	195	11	16	66	288	478	190	5	6
Bm	150	5	14	34	203	395	192	1	2
C	329	43	8	38	418	438	20	1	2
<u>Profile_3</u>									
Ah	145	9	17	49	220	445	225	4	8
Bm	145	33	12	46	236	395	159	3	2
C	301	13	6	43	363	415	52	6	1
<u>Mean</u>									
Ah	157(34)*	14(7)	21(8)	60(9)	252(34)	459(17)	207(18)	6(3)	11(8)
Bm	136(20)	17(15)	16(6)	39(6)	208(26)	395(0)	187(26)	3(2)	4(4)
C	314(14)	21(9)	6(2)	38(5)	379(34)	423(13)	44(20)	4(3)	1(1)

*Numbers in the parentheses represent standard deviations.

Appendix C-2. Concentration (ppm) of phosphorus forms in the Beaverhills series

Horizon	Ca-P	Al-P	Fe-P	Occl-P	Total Forms	Total P	Residual+ organic P	Olsen P	Miller & Axley P
<u>Profile_1</u>									
Ah	94	7	18	64	183	725	542	5	4
Bm	80	6	14	17	117	260	143	2	1
C	223	7	4	11	245	375	130	2	1
<u>Profile_2</u>									
Ah	86	20	34	109	248	930	681	8	6
Bm	113	8	36	49	206	415	209	1	2
C	281	7	2	9	299	415	116	1	trace
<u>Profile_3</u>									
Ah	83	11	18	55	167	775	608	7	2
Bm	157	2	26	55	240	375	135	trace	trace
C	318	4	3	27	352	425	73	1	trace
<u>Mean</u>									
Ah	88(6)	13(7)	23(9)	76(29)	200(44)	810(107)	610(70)	7(2)	4(3)
Bm	117(39)	5(3)	25(11)	40(20)	187(64)	350(80)	163(41)	1(1)	1(1)
C	274(48)	6(2)	3(1)	16(9)	299(54)	405(25)	106(30)	1(1)	trace

Appendix C-3. Concentration (ppm) of phosphorus forms in the Breton series

Horizon	Ca-P	Al-P	Fe-P	Occl-P	Total Forms	Total P	Residual+ organic P	Olsen P	Miller & Axley P
<u>Profile_1</u>									
Ae	57	61	107	90	315	385	70	13	36
Bt	107	2	30	32	171	250	79	1	2
C	222	23	46	59	350	438	88	4	5
<u>Profile_2</u>									
Ae	24	5	21	40	90	185	95	2	6
Bt	98	6	47	57	208	308	100	1	2
C	340	2	4	22	368	478	110	trace	trace
<u>Profile_3</u>									
Ae	33	6	36	50	125	230	105	3	9
Bt	63	1	16	40	120	202	82	trace	1
C	324	8	3	30	365	488	123	trace	trace
<u>Mean</u>									
Ae	38(17)	24(32)	55(46)	60(26)	177(121)	267(105)	90(18)	6(6)	17(16)
Bt	89(23)	3(3)	31(16)	43(13)	166(44)	253(53)	87(11)	1(0)	2(1)
C	295(64)	11(11)	18(25)	37(20)	361(10)	468(26)	107(18)	2(1)	2(1)

- x -

Appendix C-4. Concentration (ppm) of phosphorus forms in the Boundary series

Horizon	Ca-P	Al-P	Fe-P	Occl-P	Total Forms	Total P	Residual+ organic P	Olsen P	Miller & Axley P
<u>Profile 1</u>									
Ae	12	33	130	99	274	455	181	8	21
Bt	4	6	101	110	221	455	234	trace	3
C	7	8	209	173	397	500	103	trace	2
<u>Profile 2</u>									
Ae	10	4	45	77	136	275	139	1	3
Bt	5	3	101	94	203	295	92	trace	1
C	4	4	135	105	248	395	147	trace	1
<u>Profile 3</u>									
Ae	16	19	113	135	283	455	172	3	9
Bt	6	7	139	90	242	500	258	trace	2
C	11	7	237	115	370	568	198	trace	2
<u>Mean</u>									
Ae	13(3)	19(14)	96(45)	104(29)	231(83)	395(104)	164(22)	4(4)	11(9)
Bt	5(1)	5(2)	114(22)	98(11)	222(20)	417(108)	195(90)	trace	3(2)
C	7(4)	6(2)	194(53)	131(37)	338(79)	488(87)	149(48)	trace	2(1)

Appendix C-5. Concentration (ppm) of phosphorus forms in the Heart series

Horizon	Ca-P	Al-P	Fe-P	Occl-P	Total forms	Total P	Residual+ organic P	Olsen P	Miller & Axley P
<u>Profile_1</u>									
Ae	1	7	5	1	14	18	4	1	2
Bf	52	298	241	171	762	775	13	20	56
C	63	42	129	212	446	438	-8	16	25
<u>Profile_2</u>									
Ae	1	6	5	1	13	18	5	4	7
Bf	48	150	160	102	460	478	18	18	20
C	106	13	38	48	205	220	15	5	12
<u>Profile_3</u>									
Ae	2	4	4	1	12	18	6	2	3
Bf	5	746	379	155	1285	1395	110	24	84
C	45	26	79	75	225	260	35	8	20
<u>Mean</u>									
Ae	1(1)	6(2)	5(0)	1(0)	13(1)	18(0)	5(1)	2(2)	3(3)
Bf	35(26)	398(310)	260(111)	143(36)	836(417)	883(476)	47(55)	21(3)	53(32)
C	71(31)	27(14)	82(46)	112(88)	292(134)	306(116)	17(18)	10(6)	19(7)

Appendix D-1. Chemical properties of the Maleb series

Horizon	pH in soil paste	pH in 0.01M CaCl ₂	Free Fe ₂ O ₃ %	CaCO ₃ equivalent %	Fe ₂ O ₃ %	Al ₂ O ₃ %	CaO %
<u>Profile 1</u>							
Ah	6.7	6.4	.61	.14	3.29	9.73	1.15
Bm	7.0	6.8	.90	.02	4.29	10.74	1.02
C	8.0	7.9	.80	3.39	2.81	10.58	2.28
<u>Profile 2</u>							
Ah	6.9	6.7	.57	.16	2.62	8.98	1.04
Bm	7.1	6.9	.93	.04	3.50	10.87	1.15
C	8.1	7.9	.86	3.36	2.86	10.02	2.45
<u>Profile 3</u>							
Ah	7.3	7.0	.67	.03	2.92	8.88	1.12
Bm	7.3	7.0	.80	.06	3.29	10.30	1.16
C	8.0	7.9	.84	3.49	3.07	9.73	2.38
<u>Mean</u>							
Ah	7.0(.3)*	6.7(.3)	.62(.05)	.11(.07)	2.94(.34)	9.20(.46)	1.10(.06)
Bm	7.1(.2)	6.9(.1)	.88(.07)	.04(.02)	3.69(.53)	10.64(.30)	1.11(.08)
C	8.0(.1)	7.9(.0)	.83(.03)	3.41(.07)	2.92(.14)	10.11(.43)	2.37(.08)

*Numbers in the parentheses represent standard deviations.

Appendix D-2. Chemical properties of the Beaverhills series

Horizon	pH in Soil paste	pH in 0.01M CaCl ₂	Free Fe ₂ O ₃ %	CaCO ₃ equivalent %	Fe ₂ O ₃ %	Al ₂ O ₃ %	CaO %
<u>Profile_1</u>							
Ah	6.2	5.9	.93	.09	2.14	10.87	1.32
Bm	6.4	6.0	.93	.04	3.50	10.74	.92
C	7.4	7.2	1.00	1.82	3.58	10.87	1.96
<u>Profile_2</u>							
Ah	6.3	6.0	1.14	.04	3.63	11.15	1.37
Bm	6.3	6.1	1.04	.05	4.66	14.36	.95
C	7.8	7.7	.83	4.92	2.81	10.58	3.04
<u>Profile_3</u>							
Ah	6.1	5.9	1.07	.14	2.43	10.87	1.16
Bm	6.3	6.1	1.72	.14	3.22	13.19	.92
C	7.7	7.5	.96	4.16	3.00	10.02	3.08
<u>Mean</u>							
Ah	6.2(.1)	5.9(.1)	1.05(.11)	.09(.05)	2.73(.79)	10.96(.16)	1.28(.11)
Bm	6.3(.1)	6.1(.1)	1.23(.43)	.08(.06)	3.79(.77)	12.76(1.85)	.93(.02)
C	7.6(.2)	7.5(.3)	.93(.09)	3.63(1.62)	3.13(.40)	10.49(.43)	2.69(.64)

Appendix D-3. Chemical properties of the Breton series

Horizon	pH in soil	pH in paste	pH in 0.01M CaCl ₂	Free Fe ₂ O ₃ %	CaCO ₃ equivalent %	Fe ₂ O ₃ %	Al ₂ O ₃ %	CaO %
<u>Profile 1</u>								
Ae	5.2		4.6	.80	.15	1.85	8.88	.62
Bt	4.5		4.3	1.10	.01	2.92	10.58	.72
C	5.6		5.4	1.07	.02	3.07	11.06	1.15
<u>Profile 2</u>								
Ae	5.0		4.5	.71	.07	1.94	8.13	.56
Bt	4.3		4.2	1.33	.04	4.29	13.70	.82
C	7.5		7.4	1.10	3.29	3.43	11.15	2.38
<u>Profile 3</u>								
Ae	5.3		5.0	.75	.12	3.15	9.45	.70
Bt	5.0		4.9	1.14	.04	2.92	12.00	.80
C	7.3		7.2	1.16	.96	3.07	11.81	1.64
<u>Mean</u>								
Ae	5.2(.2)	4.7(.3)		.75(.04)	.11(.04)	2.31(.73)	8.82(.66)	.63(.07)
Bt	4.6(.4)	4.5(.4)		1.19(.12)	.03(.02)	3.38(.79)	12.09(1.56)	.78(.05)
C	6.8(1.0)	6.7(1.1)		1.11(.05)	1.42(1.68)	3.19(.21)	11.34(.41)	1.72(.64)

Appendix D-4. Chemical properties of the Boundary series

Horizon	pH in soil paste	pH in 0.01M CaCl ₂	Free Fe ₂ O ₃	CaCO ₃ equivalent %	Fe ₂ O ₃ %	Al ₂ O ₃ %	CaO %
<u>Profile 1</u>							
Ae	4.6	3.9	1.43	.08	2.76	8.41	.31
Bt	4.4	3.8	1.72	.06	4.29	12.95	.22
C	4.2	3.6	2.16	.04	5.53	16.92	.15
<u>Profile 2</u>							
Ae	4.6	4.1	.82	.05	2.56	8.13	.35
Bt	4.5	4.0	1.16	.08	3.13	10.87	.37
C	4.3	3.8	1.29	.09	3.89	13.42	.27
<u>Profile 3</u>							
Ae	4.9	4.3	1.07	.11	2.56	8.09	.34
Bt	4.4	4.0	1.65	.04	4.68	14.18	.24
C	4.1	3.7	1.32	.09	6.15	14.18	.20
<u>Mean</u>							
Ae	4.7(.2)	4.1(.2)	1.11(.31)	.08(.03)	2.63(.12)	8.21(.17)	.33(.02)
Bt	4.4(.1)	3.9(.1)	1.51(.30)	.06(.02)	4.03(.81)	12.67(1.67)	.28(.08)
C	4.2(.1)	3.7(.1)	1.59(.49)	.07(.03)	5.19(1.11)	14.84(1.81)	.21(.06)

Appendix D-5. Chemical properties of the Heart series

Horizon	pH in soil paste	pH in 0.01M CaCl ₂	Free Fe ₂ O ₃ %	CaCO ₃ equivalent %	Fe ₂ O ₃ %	Al ₂ O ₃ %	CaO %
<u>Profile_1</u>							
Ae	3.8	3.5	.14	trace	.33	3.12	.15
Bf	5.7	4.9	.90	.10	1.77	5.01	.18
C	5.1	4.7	1.26	.03	3.14	7.56	.41
<u>Profile_2</u>							
Ae	4.6	4.0	.11	.01	.29	2.74	.18
Bf	5.6	4.9	.84	.06	1.43	4.35	.22
C	6.0	5.3	.57	trace	1.37	4.12	.24
<u>Profile_3</u>							
Ae	4.2	3.5	.23	trace	.37	2.84	.20
Bf	5.3	4.7	1.00	.20	1.49	2.39	.27
C	5.4	4.6	.77	trace	1.77	4.57	.27
<u>Mean</u>							
Ae	4.2(.4)	3.7(.3)	.16(.06)	trace	.33(.04)	2.90(.17)	.18(.03)
Bf	5.5(.2)	4.8(.1)	.91(.08)	.12(.07)	1.56(.18)	3.92(1.36)	.22(.04)
C	5.5(.5)	4.9(.4)	.87(.36)	.01(.01)	2.09(.93)	5.42(1.87)	.31(.09)

Appendix E. Legal locations of the soil series

Soil series	Profile 1	Profile 2	Profile 3
Maleb	NE 36-11-17-W4	NE 36-11-17-W4	NW 31-11-16-W4
Beaverhills	NE 22-48-21-W4	NE 23-48-21-W4	SE 25-48-21-W4
Rimbey	SW 7-56-23-W4	-	-
Winterburn	NW 32-51-1-W5	-	-
Glory	NW 22-51-2-W5	-	-
Breton	SW 3-48-27-W4	SE 5-48-27-W4	SW 13-48-28-W4
Boundary	-- 25-83-4-W6	-- 26-83-4-W6	-- 26-83-4-W6
Heart	-- -- 60-15-W5	-- -- 60-15-W5	-- -- 60-15-W5

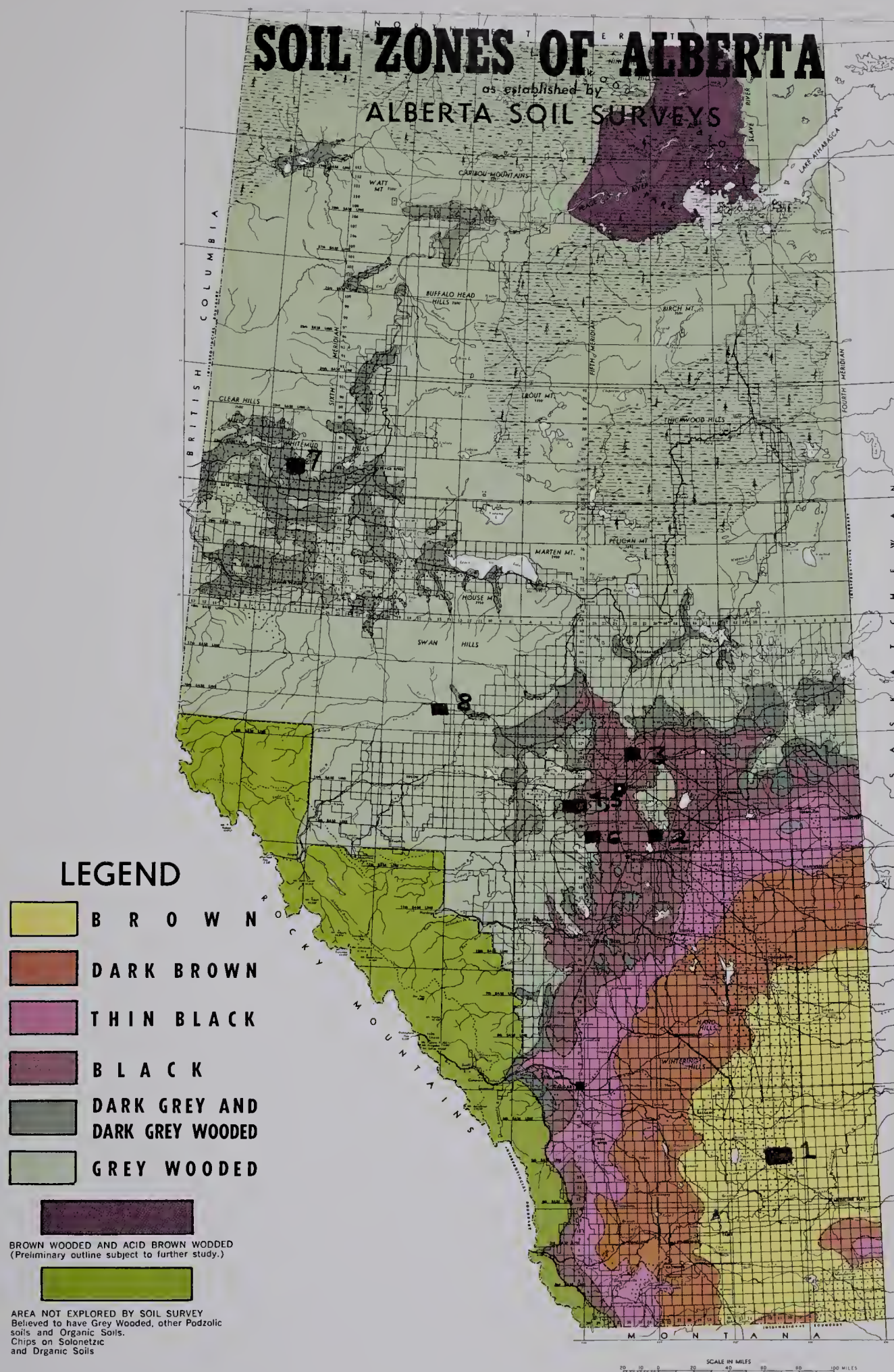


Figure 1—Soil zones of Alberta

Appendix F. Locations of the soil series

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